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Technical Report 83

THE CRYSTAL AND MOLECULAR STRUCTURE
OF ORTHORHOMBIC SULFUR

Technical Report 84

THE CRYSTAL STRUCTURE OF α -POTASSIUM SUPEROXIDE

Technical Report 85

CRYSTALLOGRAPHY OF THE TELLURIUM-IODINE SYSTEM

Technical Reports 83 to 85
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The Crystal and Molecular Structure of Orthorhombic Sulfur

by

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Laboratory for Insulation Research
Massachusetts Institute of Technology
Cambridge, Massachusetts

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THE CRYSTAL AND MOLECULAR STRUCTURE OF
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Abstract: The lattice constants of orthorhombic sulfur have been determined as $a = 10.437 \pm 0.010$, $b = 12.845 \pm 0.010$, and $c = 24.369 \pm 0.010$ Å. Using MoK α radiation, and both Weissenberg and precession cameras, 669 out of a possible 1049 structure factors have been measured. Warren and Burwell's approximation to the structure was refined first by double Fourier series, and then by repeated least-squares analyses using all the measured structure factors. The coordinates thus obtained, after the least-squares method had completely converged, were used in evaluating a triple Fourier series. The arithmetic mean of the coordinates obtained by the triple-Fourier series and the final least-squares analysis correspond to an S₈ molecule in which the average sulfur-sulfur bond length is 2.039 ± 0.007 Å, the average sulfur-sulfur-sulfur bond angle is $107^{\circ}41' \pm 39'$ and the average dihedral angle is $99^{\circ}44' \pm 48'$. There are no unusual intermolecular contacts. The dimensions in the S₈ molecule are briefly discussed in terms of other recent determinations of sulfur compounds.

1. Introduction

The crystal structure of orthorhombic sulfur was first determined by Warren and Burwell (1935) and found to consist of symmetrically puckered S₈ ring molecules. Using an elegantly simple method for reducing the number of

parameters in the problem from 12 to 2, the positional parameters were refined by the trial and error method until satisfactory agreement was obtained between the 42 observed and calculated amplitudes. The resulting arrangement led to an average sulfur-sulfur bond length of 2.12A and sulfur-sulfur-sulfur angle of 105.4° .

A re-examination of Warren and Burwell's structure was made by Ventriglia (1951), who confirmed the original solution to be correct by the use of double Patterson series. He also suggested that the sulfur-sulfur bond distances are about 2.1A and the sulfur-sulfur-sulfur angles about 105° .

The importance of an accurate knowledge of this sulfur-sulfur bond distance to current discussion concerning the presence of double-bond character in similar bonds, suggested that a new investigation be undertaken. Accordingly, all the reflections observable with molybdenum radiation have been measured, and the resulting 669 structure factors were used in three-dimensional least-squares and triple-Fourier series to determine the positional parameters.

2. Crystal Data

Orthorhombic sulfur, S_8 ; mol. wt. 256.48; transforms at 95.5°C to monoclinic sulfur and melts at 118.95° ; $D_{\text{obs}} = 2.069 \text{ gcm}^{-3}$ (Batuecas and Losa, 1951); $D_{\text{calc}} = 2.085 \text{ gcm}^{-3}$. The lattice constants were redetermined using precession photographs corrected for film shrinkage; the orthorhombic unit cell had $a = 10.437 \pm 0.010$, $b = 12.845 \pm 0.010$ and $c = 24.369 \pm 0.010\text{A}$ (Warren and Burwell's values were 10.48, 12.92 and 24.55A); (hkl) present only when $h + k$, $k + l$, $l + h = 2n$; $(0kl)$ only when $k + l = 4n$; $(h0l)$ only when $h + l = 4n$; $(hk0)$ only when $h + k = 4n$. Space group D_{2h}^{24} - Fddd. Sixteen molecules per unit cell. Molecular symmetry required; C_2 . Absorption coefficient for MoK α X radiation ($\lambda = 0.7107\text{A}$) = 20.7 cm^{-1} . Volume of the unit cell, 3266.9A^3 . Total number of electrons per unit cell, $F(000) = 2048$.

3. Intensity Measurements and Preparation

In order to minimize the introduction of error due to absorption and to a sharp termination of the experimental data, MoK α radiation was used for all measurements. Small, regular-shaped crystals were grown from carbon disulfide solution, and found to be quite stable under X irradiation for many weeks. Precession and a modified equi-inclination Weissenberg camera (Abrahams, 1954) techniques were employed to obtain the photographic records. Visual intensity measurements were made using both multiple exposure and multiple film methods. In the latter, sheets of 1-mil nickel foil were interleaved between films (Ilford "Industrial-G" was used almost exclusively) and the resulting intensity reduction in an X-ray beam passing through one thickness of film and foil was determined to be 3.4 to 1 by Geiger-counter measurement. Five crystals were used, varying in size from 0.12x0.12x0.25 mm to 0.30x0.15x0.30 mm. The ratio of the strongest to the weakest intensity in any layer was about 1000 to 1. The entire reciprocal lattice was explored by recording the intensities of the hk0, hkl, hk2, hk3, and hk4 layers with a precession camera, and the h0 ℓ , h1 ℓ , h2 ℓ , h3 ℓ , h4 ℓ , h5 ℓ , h6 ℓ , h7 ℓ , 0k ℓ , 1k ℓ , 2k ℓ , 3k ℓ , 4k ℓ , 5k ℓ , 6k ℓ , 7k ℓ , 8k ℓ , hh ℓ , and parts of the h-1, h+1, ℓ , and h-2, h+2, ℓ , layers with a Weissenberg camera.

Intensities measured on the precession-camera film were corrected for the Lorentz and polarization factor using the charts of Grenville-Wells and Abrahams (1952), and those on the Weissenberg films by the usual Lorentz and polarization factors, and by the Tunell (1939) rotation factor. Absorption corrections were not made in view of the small crystals and their approximation to a spherical shape. After the intensities in each layer had been reduced to structure factors, they were placed on the same scale by using the common reflections in each pair of layers; 269 of these structure factors were observed once only, 307 were observed twice, 80 were observed three times, and 13 were obtained

four times. In the 400 cases where a given structure factor was measured more than once, the mean value was taken. These observed values for the structure factors are given in Table 8.

The multiple observation of structure factors was used to obtain a measure of the error in the mean value. Whittaker and Robinson (1944) showed that if there are n observations of F_i , the standard deviation in any observed $\sigma(F_i) = \left[\sum_i (\bar{F} - F_i)^2 \div (n - 1) \right]^{1/2}$, where $\bar{F} = \sum_i F_i \div n$. This relation clearly holds only for n large. When $n = 2, 3, 4$ the significance of $\sigma(F_i)$ becomes rather ambiguous. Nevertheless, $\sigma(F_i)$ was evaluated for all $F(hk\ell)$'s observed more than once. The average value of $\sigma(F_i)$ was then 8.7 percent of F_i , and to a rough approximation $\sigma(F_i) \div |F_i|$ is independent of the magnitude of F_i .

4. Analysis of the Structure

In the space group $Fddd$ the general position is 32-fold, and four of the sulfur atoms in this crystal lie in this position. However, by assuming the S_8 molecule to be a symmetrical puckered ring of chosen S-S bond length and S-S-S bond angle, only two parameters remain unknown. The molecule may be regarded as consisting of two squares with one turned through 45° with respect to the other; the chosen bond dimensions then determine the length of the square side and the separation of the two planes of the squares. The center of this molecule lies on a 16-fold position having only the single parameter z , and the remaining unknown is the angle made by the plane of the rings with the a axis. Having thus reduced this problem to one of two unknowns only, Warren and Burwell (1935) approximately solved them by a consideration of the 00ℓ and $hk0$ reflections. Further refinement was then sought by making small adjustments in the atomic coordinates to give better agreement among the 42 observed and calculated amplitudes, which include 14 $hk\ell$ reflections. The resulting atomic coordinates are given in Table 1, which correspond to the bond distances

$S_1-S'_1 = 2.18$, $S_4-S'_4 = 2.11$, $S_1-S_3 = 2.07$, $S_2-S_3 = 2.11$ and $S_2-S_4 = 2.12\text{\AA}$. The average S-S-S bond angle was 105.4° .

Table 1. Warren and Burwell's (1935) atomic coordinates for orthorhombic sulfur.

Origin at 222				Origin at center		
	x	y	z	x	y	z
S_1	0.983	0.083	0.072	0.858	0.958	0.947
S_2	0.906	0.161	0.200	0.781	0.036	0.075
S_3	0.833	0.105	0.125	0.708	0.980	0.000
S_4	0.906	0.028	0.250	0.781	0.903	0.125

The x and z coordinates from Table 1 were then used to compute ($h0\ell$) structure factors. (See Section 5 for the atomic form factors used.) The resulting value of $R_1 = \sum ||F_{\text{obs}}| - |F_{\text{calc}}|| \div \sum |F_{\text{obs}}|$ in this layer, using the observed structure factors in Table 8, was 0.31. After two Fourier series projections, no further sign changes were observed, and the final series is shown in Fig. 1. The coordinates obtained from Fig. 1 corresponded to $R_1 = 0.155$. The z coordinates from Fig. 1 and the y coordinates from Table 1 were then used in Fourier series projections along the a axis to refine the y coordinates, and two such projections gave Fig. 2 with all signs again having ceased to change. Here $R_1 = 0.217$. The combined coordinates from Figs. 1 and 2 are given in Table 2. The coordinates in Table 2 were then used to calculate the $hk\ell$ structure factors after first transforming to an origin at the center of symmetry. The agreement factor R_1 between the 669 observed $F(hkl)$'s and the corresponding set of calculated structure factors, using a second empirical atomic scattering curve (Section 5) at this initial stage in the three-dimensional work, was 0.258.

Three-dimensional least-squares refinement

The means chosen for refining the atomic parameters with all the reflections

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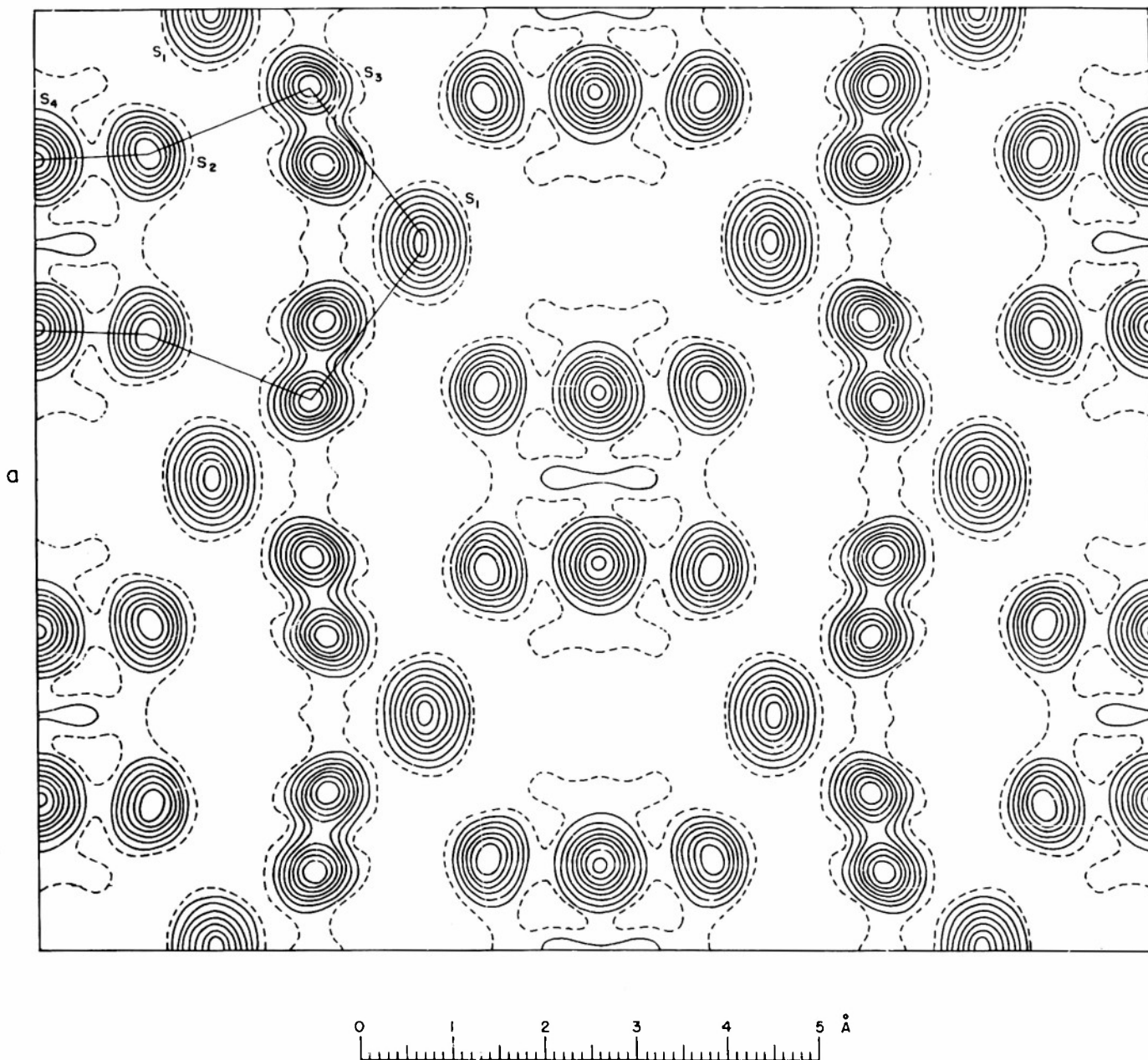


Fig. 1. Projection of one-half unit cell of orthorhombic sulfur along the b axis. Contours for atoms S_2 and S_3 are at intervals of 4 eA^{-2} ; for atoms S_1 and S_4 the interval is 8 eA^{-2} . The 4 eA^{-2} line is dotted.

c / 2

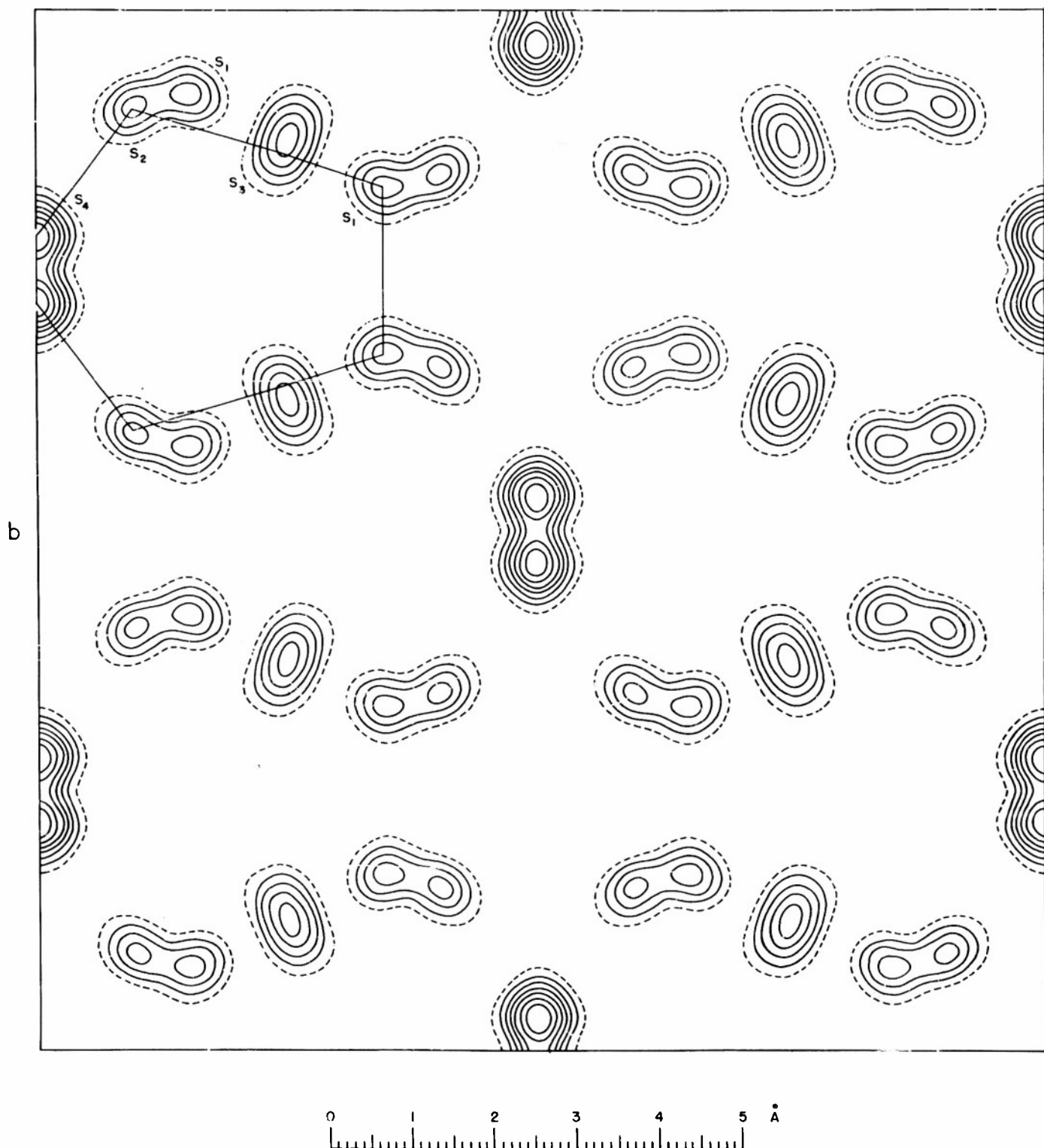


Fig. 2. Projection of one-half unit cell of orthorhombic sulfur along the c axis. All contours are at intervals of 8 eA^{-2} , the 8 eA^{-2} line being dotted.

Table 2. Atomic coordinates from Fourier series projections along the a and b axes.

Origin at 222			
	x	y	z
S ₁	0.9907	0.0810	0.0775
S ₂	0.9042	0.1549	0.2013
S ₃	0.8333	0.1122	0.1279
S ₄	0.9091	0.0326	0.2500

observable using MoK α radiation, was the method of least squares (Whittaker and Robinson, 1944; Hughes, 1941). In this method all weights were initially placed equal. An examination of various weighting schemes (Section 7) appears to justify this simplifying procedure, and hence it was adopted throughout this work. The 669 observational equations were reduced to 12 normal equations in the usual way, evaluating only the coefficients of the diagonal terms, and hence deriving the corrections ($\Delta \xi_j$) to be made to the atomic coordinates (ξ_j), by relations of the form

$$\Delta \xi_j \cdot \sum_{hkl} \left[\frac{\partial F(hkl)}{\partial \xi_j} \right]^2 = \sum_{hkl} \left[\frac{\partial F(hkl)}{\partial \xi_j} \cdot \Delta F(hkl) \right],$$

where $\Delta F(hkl) = F_{\text{obs}}(hkl) - F_{\text{calc}}(hkl)$.

The first application of this method produced a maximum shift in atomic coordinates of 0.10A, and the structure factors calculated on the basis of these corrected coordinates contained 26 with changed sign. The value of R_1 fell to 0.177. A second application produced only 3 changes in the signs of structure factors, with a maximum coordinate correction of 0.02A. A total of five applications of this technique was required before the largest value of $\Delta \xi_j < \sigma(\Delta \xi_j)$, the standard error in that $\Delta \xi_j$ (see Section 10). The respective values of $\Delta \xi_j$ and $\sigma(\Delta \xi_j)$ after the fifth least-squares process were 0.001 and 0.006A. R_1 then

became 0.162. The corresponding set of atomic coordinates is given under A, Table 3.

Table 3. Atomic coordinates of orthorhombic sulfur. Origin at center.

	A (Least squares)	B (Fourier series)	C (Arithmetic mean)
x_1	0.8562	0.8549	0.8556
y_1	0.9525	0.9523	0.9524
z_1	0.9518	0.9516	0.9517
x_2	0.7844	0.7843	0.7844
y_2	0.0305	0.0299	0.0302
z_2	0.0764	0.0762	0.0763
x_3	0.7065	0.7065	0.7065
y_3	0.9799	0.9791	0.9795
z_3	0.0040	0.0041	0.0040
x_4	0.7855	0.7861	0.7858
y_4	0.9085	0.9069	0.9077
z_4	0.1294	0.1286	0.1290

Triple Fourier-series determination of atomic coordinates

It was felt desirable to check the final coordinates obtained by the least-squares method, using an independent route. Two common alternatives were considered: the differential synthesis and the triple Fourier-series methods. The former was rejected because of the inherent uncertainty in the meaning of electron density maxima if the profile is asymmetric. Figure 3 illustrates this source of error in the use of such turning-point methods. Since the final least-squares coordinates were, at worst, very close to the true values, the electron density along lines parallel with each axis and passing through these coordinates was computed, i. e., $(x_j + \Delta x, y_j, z_j)$, etc., were evaluated for known steps of

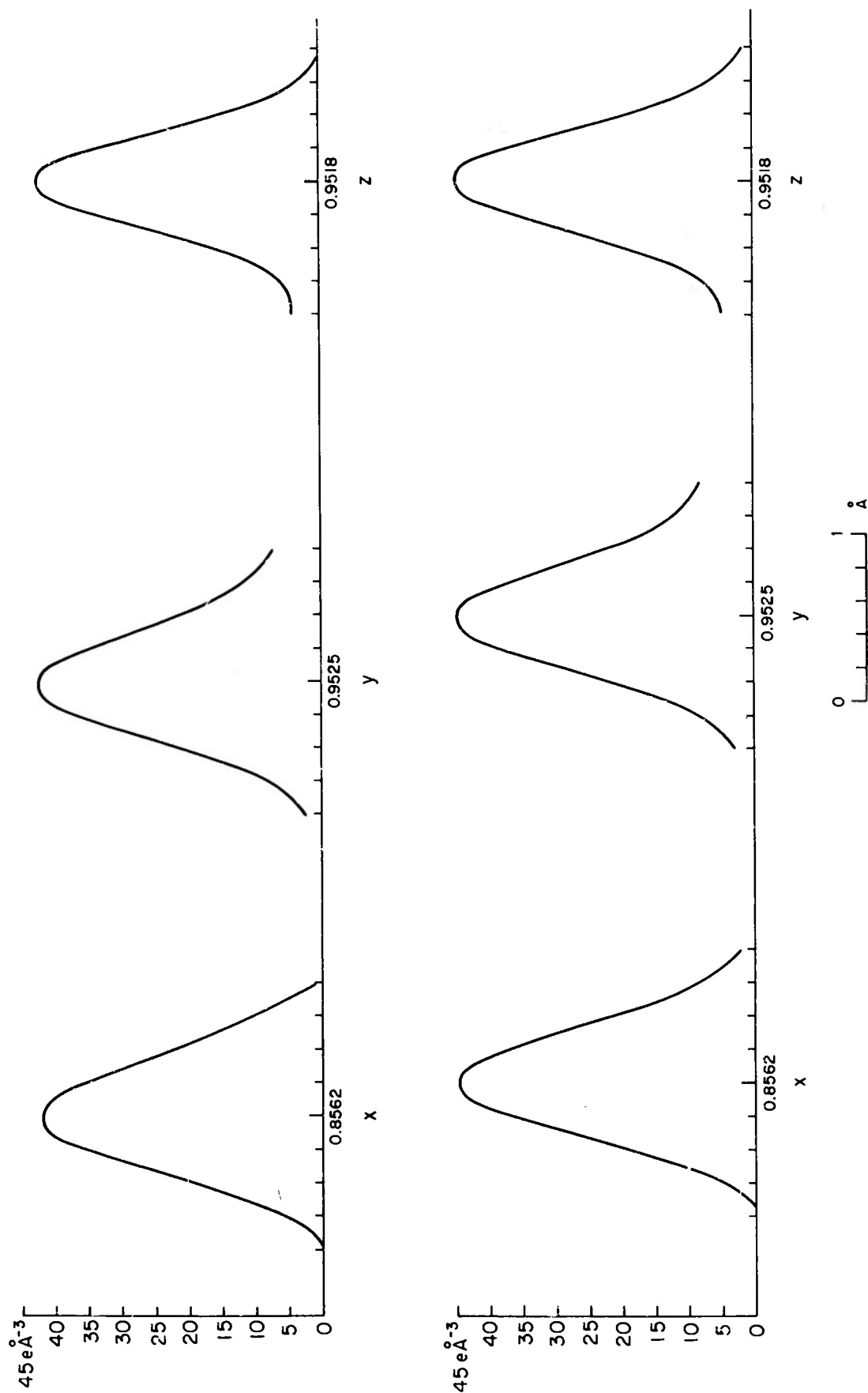


Fig. 3. Electron density profile of atom S_1 along lines parallel with the a, b and c axes. The upper profiles have been computed with F_{meas} as the coefficients in the triple Fourier series, the lower profiles with F_{calc} . The coordinates marked are those found by the least-squares method.

Δx , as in Fig. 3.

The center of gravity of this profile was taken as coincident with the atomic coordinate along the line of the profile. Experience suggests that coordinates obtained in this manner are insensitive to small displacements of these lines. Each atomic electron density profile was evaluated twice, once with the observed structure factors and then with the structure factors calculated on the basis of the final least-squares coordinates as the coefficients in the triple Fourier series. Corrections could thus be made in the usual way $\left[\xi_{\text{correct}} = \xi_{\text{observed}} + (\xi_{\text{obs}} - \xi_{\text{calc}}) \right]$ for errors introduced into the triple Fourier series using the observed $F(hk\ell)$ values, due to series termination. The corrected set of atomic coordinates thus obtained are given under B, Table 3.

5. Atomic Form Factors

James and Brindley's (1931) atomic form factor for sulfur was used at first, modified by a temperature factor $B = 3.25A^2$, in the expression $\exp \left[-B \left(\frac{\sin \theta}{\lambda} \right)^2 \right]$. This value was obtained by a consideration of the limiting value of $\frac{\sin \theta}{\lambda}$ at which $(h0\ell)$ reflections ceased to be observable. Structure factors, based upon this temperature factor-modified curve together with the atomic coordinates in Table 1, hence permitted the observed structure factors to be placed upon a scale close to absolute. With this scale a first empirical atomic scattering factor curve was derived, using the relation $f(h0\ell) = F(h0\ell)_{\text{abs}} \div 32 \sum_j \cos 2\pi h x_j \cdot \cos 2\pi \ell z_j$. The values of $f(h0\ell)$ thus obtained were plotted against $2 \sin \theta$ and a mean value of f was found for each interval of $2 \sin \theta = 0.1$. A smooth curve was then drawn through these mean values; this is the form factor used in obtaining $R_1(h0\ell) = 0.31$ in Section 4.

All the observed structure factors were then placed on the same scale as the final set of observed $(h0\ell)$ and $(0k\ell)$ structure factors after completion of the double Fourier series refinement process. A second empirical atomic form-

factor curve was derived by $f(hk\ell) = F(hk\ell)_{\text{abs}} \div G(hk\ell)$, where $G(hk\ell)$, the geometrical part of the calculated structure factor, was used only if greater than 10 (maximum value is 128), and was based upon the coordinates in Table 2. A smooth curve was drawn, as described previously.

After three least-square cycles had been completed, a third and final f curve was derived. The absolute scale was this time determined by Wilson's (1942) method, and the previous scale was found to be 5.1 percent too high. After adjustment to the Wilson scale, the new f curve was extracted in the same way as the second empirical curve, the atomic coordinates from the third least-squares process being used to compute $G(hk\ell)$. Since the absolute scale was not directly measured by an absolute experimental method, it is possible that the final scale of the f curve reproduced in Fig. 4 might be in error. Such an error is thought to be not more than about 5 percent. The temperature factor, determined by Wilson's method, based on the James and Brindley f curve at the same time as the absolute scale, was 3.46\AA^2 . For comparison, the James and Brindley f curve (with $B = 3.25\text{\AA}^2$) and also the empirical f curve found by Cox, Gillot and Jeffrey (1949) for thiophene are given in Fig. 4.

6. Anisotropy in the Thermal Vibrations

The empirical scattering curve (Fig. 4) used in the final determination of the atomic coordinates gives the efficacy of X-ray scattering by the sulfur atoms undergoing certain thermal vibrations. The absolute value of the amplitude of this vibration has not been determined, but has been assumed equal in all directions. The validity of assuming isotropic thermal motion may be tested by replacing $f(hk\ell)$ for each j th atom by $f(hk\ell) \exp -[\alpha_j h^2 + \beta_j k^2 + \gamma_j \ell^2]$ (James, 1950). In this expression, α_j , β_j , and γ_j are corrections to the overall temperature factor implicit in the curve of Fig. 4 for each j th atom in directions parallel with the a , b , and c axes, respectively. The structure factor expression thus

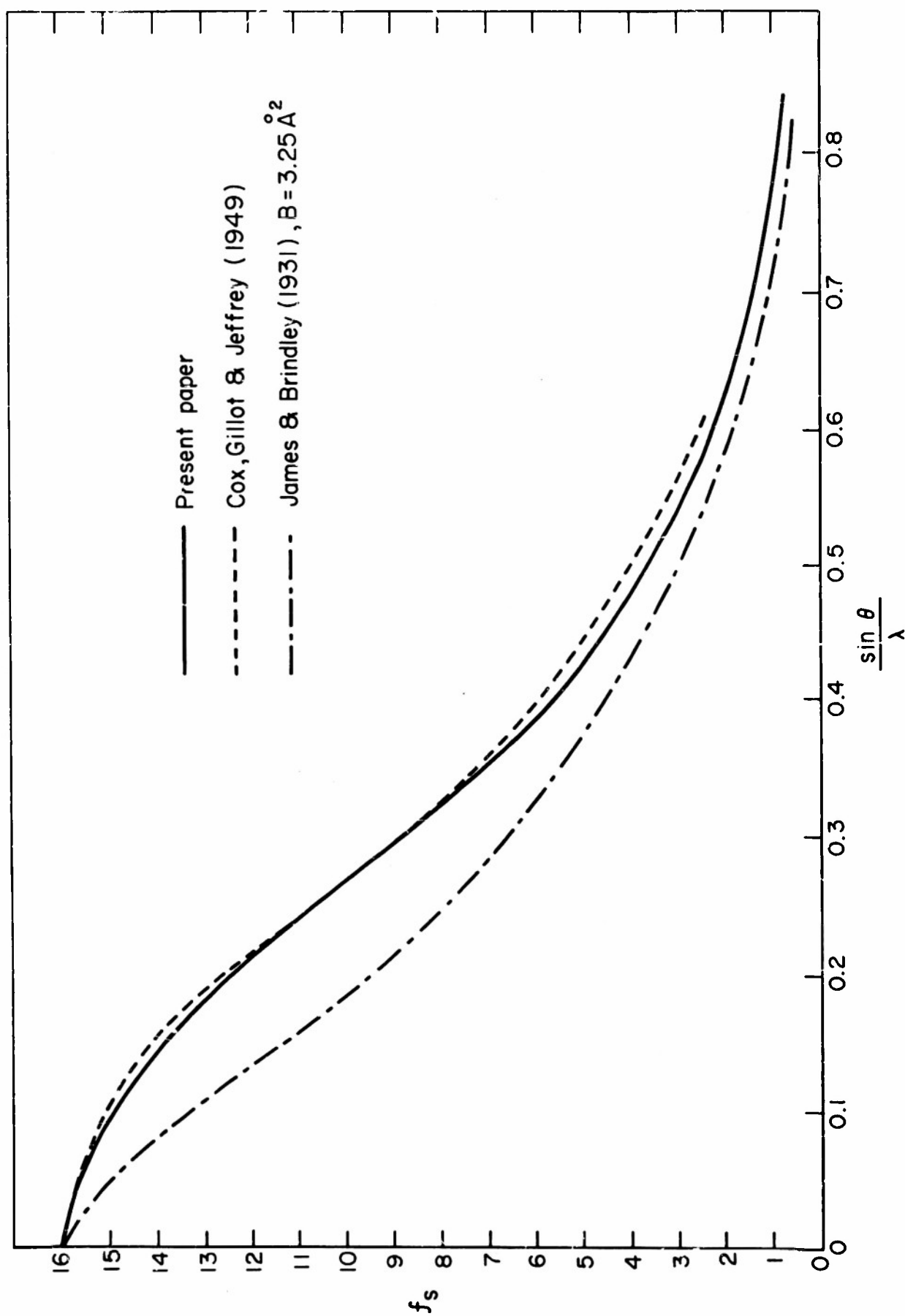


Fig. 4. Atomic scattering curves for sulfur.

$$\text{becomes } F(hk\ell) = f(hk\ell) \sum_{j=1}^4 G_j(hk\ell) \exp - [a_j h^2 + \beta_j k^2 + \gamma_j \ell^2] .$$

Evaluation of these corrections was made by the method of least squares, using the coordinates under A, Table 3. It was assumed that, to a close approximation, the values of a_j , β_j , γ_j are independent of further changes in the $\Delta \xi_j$'s. Diagonal terms only of the form $\sum \left[\frac{\partial F(hk\ell)}{\partial a_j} \right]^2 \cdot \Delta a_j = \sum \left[\frac{\partial F(hk\ell)}{\partial a_j} \cdot \Delta F(hk\ell) \right]$ were computed, and resulted in the values given in Table 4. The stand-

Table 4. Values of the correction to the empirical isotropic temperature factor.

	α	β	γ
S_1	- 0.00010	- 0.00069	- 0.00013
S_2	- 0.00025	- 0.00022	- 0.00003
S_3	- 0.00027	- 0.00008	- 0.00008
S_4	- 0.00030	+ 0.00009	- 0.00005

ard deviations in these corrections had the following average values: $\sigma(\overline{a_j}) = 0.0005$, $\sigma(\overline{\beta_j}) = 0.0003$ and $\sigma(\overline{\gamma_j}) = 0.0003$, which are very similar to the actual values observed in Table 4. Nevertheless, these values were used in computing a new set of structure factors. This set changed R_1 from 0.162, corresponding to the coordinates under A, Table 3, to 0.161. The scarcely significant reduction in R_1 , together with the magnitude of the standard deviation in the a_j , β_j , γ_j suggest that indeed there is an isotropic and equal thermal motion for each atom. A simple experimental observation supporting this suggestion is that in each Weissenberg photograph, for each layer recorded, there is a very uniform value of $\sin \theta$ at which reflections cease to be observable.

7. The Weighting Factor

In the correct use of the method of least squares, each observation should be properly weighted so that each equation of condition possesses equal weight.

Each weight is proportional to the square of the moduli of precision of the observation, $h(F)$ (Whittaker and Robinson, p. 223). Further, $\sigma(f) = 1/\left[\sqrt{2} h(F)\right]$, and hence by computing the standard error in each structure factor, the correct weight should readily be assignable. However, in most crystal structure determinations, $\sigma(F)$ cannot properly be obtained, due to the small experimental sampling of the value of each structure factor. In recognizing this difficulty, several other weighting schemes have been adopted in the literature, and some of these are examined here. In all the following schemes the coordinates under A, Table 3, were used in evaluating F_{calc} , and hence the $\Delta F(hk\ell)$ terms required in the equations of condition:

- a) The approximate standard deviation in the structure factors were used, calculated as in Section 3, viz., $\sqrt{w}(hk\ell) = 1/\sigma(F(hk\ell))$
- b) Since the approximate $\sigma F(hk\ell)$'s are roughly proportional to $|F(hk\ell)|$, i. e., $\sigma F(hk\ell) \simeq 0.087 |F(hk\ell)|$; $\sqrt{w}(hk\ell)$ was taken equal to $1/\left[0.087 |F(hk\ell)|\right]$
- c) The assumption of proportionality of the standard deviation with the magnitude of the structure factor is most violated for $|F(hk\ell)| < 100$. Also within this range, lies the majority of the structure factors (Fig. 5). Hence for all $|F(hk\ell)| < 100$, a weight of 0.010 was used, and for $|F(hk\ell)| > 100$ weights were as in b)
- d) It was suggested by Cruikshank and Robertson (1953) that $\Delta F(hk\ell)$ could be used as $\propto 1/\sqrt{w}(hk\ell)$.

In Cases a, b, and c, the correction to the atomic coordinates in many cases exceeded the standard error in that correction by as much as a factor of 8. The corresponding shifts in the atomic coordinates had a maximum of about 0.04A, and in all these cases resulted in maximum differences in S-S bond lengths of as much as 0.13A. In Case c) the value of R_1 was calculated and found to be 0.209. In Case d), every $\Delta \xi_j \leq \sigma(\Delta \xi_j)$.

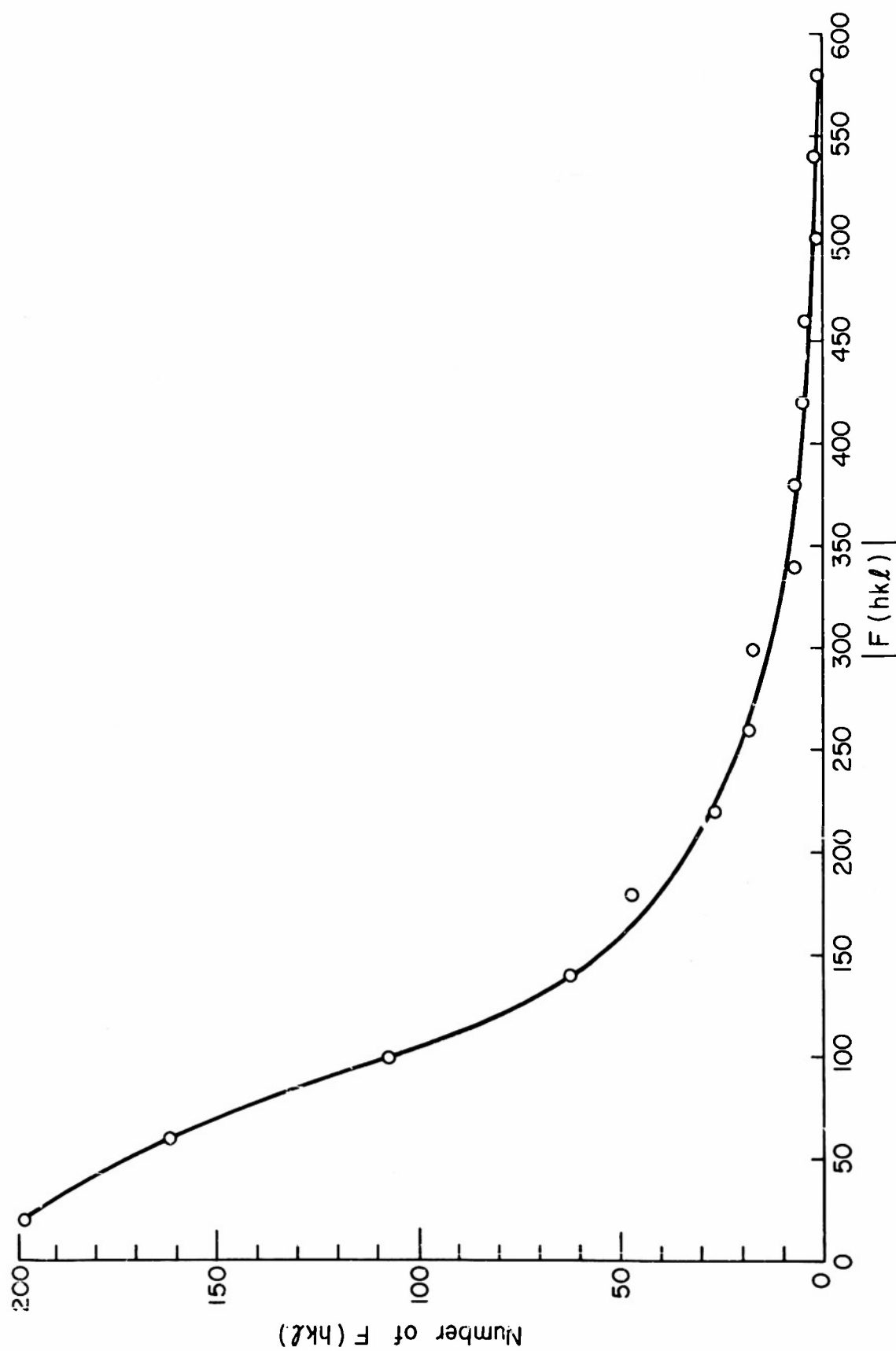


Fig. 5. Distribution of magnitudes of F_{meas} .

It thus appears that none of the four weighting schemes investigated is of practical value in applying the method of least squares to crystal structure determinations, provided all the structure factors are measured with equal care and that the ratio of number of observational equations to parameters is large. The initial scheme of placing all weights equal to unity was hence used in the final determination of atomic coordinates by the least-squares method.

8. Final Coordinates

The coordinates obtained from the final least-squares treatment of Section 4 are under A, Table 3; those from the triple Fourier series method, corrected for termination of the series by Booth's (1947) method, under B. These corrections were small with a maximum value of 0.007A and a root mean-squares value of 0.003A. The arithmetic mean (column C) of these two sets of coordinates is taken as the final set. Structure factors, based on column C, Table 4, and the empirical scattering curve in Fig. 3, assuming no anisotropy in the thermal vibrations, are given in Table 8 under F_{meas} .

9. Molecular Dimensions

The coordinates under C, Table 3, correspond to the bond distances and angles in Table 5.

Table 5. Bond distances and angles.

$S_1-S'_1 = 2.027\text{A}$	$S'_1 S_1 S_3 = 108^\circ 36'$	Average S-S = 2.039A Average S-S-S = $107^\circ 41'$
$S_4-S'_4 = 2.043$	$S_3 S_2 S_4 = 107^\circ 30'$	
$S_1-S_3 = 2.042$	$S_1 S_3 S_2 = 106^\circ 47'$	
$S_2-S_4 = 2.032$	$S'_4 S_4 S_2 = 108^\circ 57'$	
$S_2-S_3 = 2.047$		

Since the distances $S_1-S'_1$ and $S_4-S'_4$, lie across a two-fold axis, they have only half the weight of the other three distances. Similarly, the angles $S'_1 S_1 S_3$ and

$S'_4 S_4 S_2$ have half the weight of the other two angles. With these weights, the average S-S distance is 2.039A and the average S-S-S angle is $107^{\circ}41'$.

The S_8 molecule in this crystal may be described as consisting of two "squares" formed by atoms $S_1 S_2 S'_3 S'_4$ and $S_1 S_2 S_3 S'_4$, with a distance of 0.99A between their mean planes. One "square" is turned through 45° with respect to the other, and their two planes are identically parallel. The average length of the side of the "square" is 3.299A, and the average angle is $90^{\circ}2'$; the individual lengths and angles are shown in Fig. 6. The atoms in the "square" have a R.M.S. deviation of 0.030A from their mean plane.

There are three different dihedral angles in this molecule, as given in Table 6.

Table 6. Dihedral angles in S_8

$S_1 S_2 S_3 / S_2 S_3 S_4 = 100^{\circ}45'$
$S_1 S_2 S_3 / S'_1 S_1 S_3 = 98^{\circ}55'$
$S_3 S_2 S_4 / S_2 S_4 S'_4 = 98^{\circ}31'$

The angles obtained using the primed atoms have only half the weight of the first angle. Hence the mean dihedral angle is $99^{\circ}44'$. It may be observed that if this angle were 90° , the distance between every fourth sulfur atom, keeping the average S-S distance and S-S-S angle in Table 5, would be 4.276A, whereas $S_3-S'_3$ for example is 4.425A.

10. Uncertainties in the Atomic Coordinates, Bond Lengths and Angles

The standard deviation in the corrections to the atomic coordinates is readily computed after the normal equations have been evaluated in the least-squares process, using the relation (Whittaker and Robinson, 1944)

$$\sigma(\Delta \xi_j) = \left\{ \frac{\sum v^2}{m-s} \cdot \frac{A_{11}}{D} \right\}^{1/2}, \quad (1)$$

where v is the residual, D the determinant formed by the coefficients of the normal equation, A_{11} the minor determinant of the coefficient of the correction $\Delta \xi_j$,

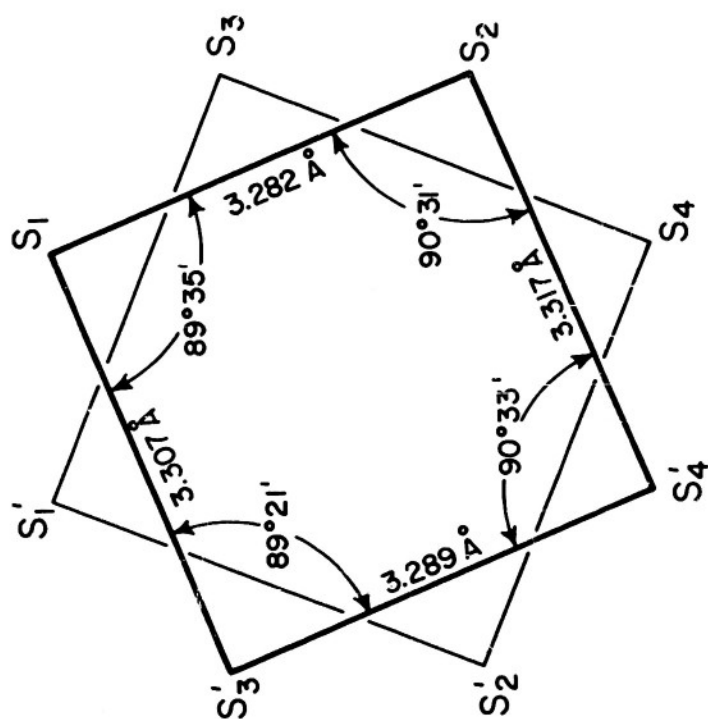
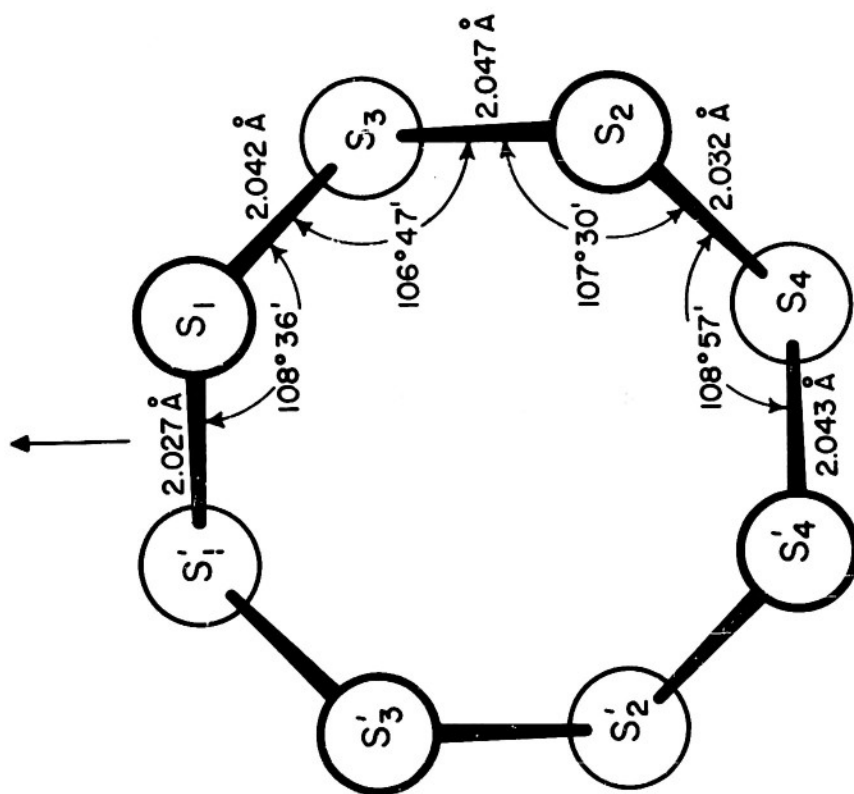


Fig. 6. Dimensions in the S_8 molecule in orthorhombic sulfur.

m the number of observational equations, and s the number of parameters.

Equation (1) may be closely approximated by

$$\sigma(\Delta \xi_j) = \left\{ \frac{\sum [\Delta F(hkl)]^2}{(m - s) \sum \left[\frac{\partial F(hkl)}{\partial \xi_j} \right]^2} \right\}^{1/2}, \quad (2)$$

and the resultant Eq. (2) was used in this work. The standard deviation of each coordinate in Ångströms was very nearly equal throughout. The standard deviation in the corrections produced by the first three-dimensional least-squares application was about 0.009Å per coordinate. The final corrections leading to Table 3, Column A had a standard deviation of about 0.0058Å per coordinate. Hence the standard deviation in the position of each atom is 0.010Å.

Cruickshank's (1949) method was also used to determine the estimated standard deviation in the atomic coordinates obtained by the triple Fourier series method (B, Table 3). Retaining his nomenclature, p_x and p_y are 4.21, p_z is 6.00; $A_{hh} = A_{kk}$ is 209.2, A_{ll} is 507.5 eA^{-5} ; $\sigma(A_h)$ is 1.609; $\sigma(A_k)$ is 1.511; and $\sigma(A_l)$ is 1.796 eA^{-4} . Thus $\sigma(x) = 0.008A$, $\sigma(y) = 0.007A$, and $\sigma(z) = 0.004A$, so that the estimated standard deviation in the position of each atom by Cruickshank's method is 0.011Å.

The mean value of the standard deviation in the coordinate of each atom is thus taken to be 0.010Å, and hence in any one S-S bond is 0.014Å. However, this bond length is measured independently four times, in the S_8 molecule. The arithmetic mean of the four S-S bond distances hence has a standard deviation of $\sigma(S-S)/\sqrt{4} = 0.007A$ (Whittaker and Robinson, 1944). The limit of error in this arithmetic mean distance can be taken as double the standard deviation, i.e., 0.014Å. It may be noticed in Table 5 that all the individual values of the S-S bond length lie within this limit of error of the arithmetic mean distance.

The standard deviation in each sulfur-sulfur-sulfur bond angle is readily

computed from the data above, to be $68'$. This angle is independently measured three times, and hence the standard deviation in the arithmetic mean of these three values is $39'$. Each of these three values lies within the limit of error, double the standard deviation, i. e., $1^{\circ}18'$ of the arithmetic mean angle (Table 5). The standard deviation in the dihedral angle is the same as in the bond angle, viz. $68'$. This angle is independently measured only twice, since two of the observations have half the weight of the other, and hence the standard error in the dihedral angle is $68'/\sqrt{2} = 48'$.

11. Intermolecular Contacts

In this crystal, there are four contacts only between atoms of neighboring molecules that are less than 4A. The shortest of these is of 3.689A between S_3' and S_2 of the molecule related by a center. The primed atom is related to the unprimed in Table 3 by the two-fold axis passing through the molecule.

12. Discussion

In any scheme of representing bond lengths in terms of corresponding bond orders, the lengths of the pure single and double bonds are of particular importance. For the case of sulfur, a scheme has been proposed in which the length of the bond of order zero is taken as 2.08A and of order unity as 1.88A, with intermediate points derived from the alternating sulfur-sulfur bond lengths found in the hexasulfide and tetrasulfide ions (Abrahams, 1954). The sulfur-sulfur distance in the S_8 molecule was examined in case it could be taken as an example of a pure single bond. However, the measured distance of 2.039A in orthorhombic sulfur appears to correspond not to a pure single bond, but to one with order 0.3, according to the scheme above.

The possibility of substantial double-bond character occurring in the S_8 molecule was suggested previously by Powell and Eyring (1943). These authors discussed the reaction $(x/8)S_8 \text{ ring} \rightarrow S_x \text{ chain}$, for which the heat of reaction

is 27.5 ± 5 kcal, in terms of the bond strength of S-S given by Pauling (1939) as 63.9 kcal.* The large energy difference between opening the eight-membered ring, and breaking a sulfur-sulfur bond was postulated as being due to the formation of some double-bond character in which the available 3d orbitals were used. Thus by taking on a certain amount of "aromatic" character, the S_8 ring could achieve appreciable stability from the consequent resonance energy. They further postulated that on opening the ring, the resulting chain might retain some of this resonance energy, and hence could account for the energy difference.

An alternative view is that the distance 2.039A really represents a pure single S-S distance, and that those bonds which are longer than this are less than single. Some support for believing the S_8 molecule does possess some double bond character can be found by considering the dihedral angles in this molecule. The average dihedral angle is $99^{\circ}44'$ while in the free polysulfide group, the average angle is ca. 78° (Abrahams, 1954). Thus, in the ring, the dihedral angle has become much flatter, indicating a tendency towards planarity in the molecule, such as would be required for the postulated "aromatic" character to become a maximum.

The sulfur-sulfur-sulfur bond angle of $107^{\circ}41' \pm 39'$ is close to other recently measured values for this angle (Table 7). This angle hence appears

Table 7. Sulfur-sulfur-sulfur bond angles.

Compound	Value	Reference
Cesium hexasulfide	$108.8 \pm 2^{\circ}$	Abrahams and Grison (1953)
Barium tetrasulfide monohydrate	$104.7 \pm 2^{\circ}$	Abrahams (1954)
Dimethanesulfonyl disulfide	$104.0 \pm 3^{\circ}$	Sørum (1953)
Barium tetrathionate dihydrate	$103.0 \pm 2^{\circ}$	Foss, Furberg and Zachariasen (1954)
Barium pentathionate dihydrate	$104.5 \pm 2^{\circ}$	Foss and Zachariasen (1954)

* A recent determination of the S-S bond strength in several alkyl disulfides (Franklin and Lumpkin, 1952) places the bond strength between 70 and 73.2 kcal.

Table 8. Measured and calculated values of the orthorhombic sulfur structure factors.

hkl	F _{meas}	F _{calc}	hkl	F _{meas}	F _{calc}	hkl	F _{meas}	F _{calc}	hkl	F _{meas}	F _{calc}	hkl	F _{meas}	F _{calc}
004	< 14	+ 4	1, 1, 25	< 36	- 9	0, 2, 18	250	+250	10, 2, 16	54	- 41	7, 3, 21	167	+127
008	216	+187	1, 1, 27	58	- 42	0, 2, 22	117	- 74	10, 2, 18	< 55	- 14	7, 3, 23	83	- 72
0, 0, 12	22	- 5	1, 1, 29	< 40	+ 31	0, 2, 26	39	+ 34	12, 2, 2	66	- 42	7, 3, 25	60	- 42
0, 0, 16	532	+548	1, 1, 31	51	+ 32	0, 2, 30	68	- 66	12, 2, 4	< 30	+ 24	7, 3, 27	< 40	+ 2
0, 0, 20	37	- 2	1, 1, 33	82	+ 69	0, 2, 34	53	+ 65	12, 2, 6	76	+ 68	7, 3, 29	41	+ 32
0, 0, 24	382	+326	1, 1, 35	< 47	- 9	0, 2, 38	< 50	+ 12	12, 2, 8	54	+ 55	7, 3, 31	< 44	+ 2
0, 0, 26	< 41	+ 4	311	316	-376	220	315	-301	12, 2, 10	77	- 79	931	< 28	+ 24
0, 0, 32	< 44	- 27	313	418	+396	222	560	-662	12, 2, 12	< 57	- 8	933	147	-150
0, 0, 36	28	- 3	315	58	+ 50	224	160	+125	12, 2, 14	58	+ 44	935	62	- 58
0, 0, 40	92	+ 75	317	356	+442	226	< 20	- 3	12, 2, 16	59	- 72	937	< 33	- 33
202	145	+ 94	319	344	+364	228	< 21	+ 13	12, 2, 18	< 60	- 32	939	110	+113
206	537	-583	3, 1, 11	164	+145	2, 2, 10	207	-205	14, 2, 0	< 29	- 10	9, 3, 11	< 34	+ 10
2, 0, 10	84	- 84	3, 1, 13	190	+180	2, 2, 12	340	+345	14, 2, 2	59	+ 99	9, 3, 13	< 35	- 17
2, 0, 14	128	+128	3, 1, 15	37	+ 69	2, 2, 14	405	-424	14, 2, 4	< 60	- 10	9, 3, 15	84	+ 78
2, 0, 18	274	+232	3, 1, 17	< 29	- 38	2, 2, 16	59	- 67	131	252	-243	9, 3, 17	< 36	- 30
2, 0, 22	235	-196	3, 1, 19	97	+ 88	2, 2, 18	46	- 25	133	270	+188	9, 3, 19	104	- 70
2, 0, 26	121	- 94	3, 1, 21	31	+ 52	2, 2, 20	43	- 36	135	376	-340	9, 3, 21	64	- 66
2, 0, 30	47	- 37	3, 1, 23	49	- 18	2, 2, 22	124	- 98	137	387	-364	9, 3, 23	39	- 41
2, 0, 34	< 60	+ 19	3, 1, 25	69	- 57	2, 2, 24	49	- 49	139	21	- 39	9, 3, 25	< 42	+ 49
400	321	+344	3, 1, 27	108	+ 76	2, 2, 26	119	- 94	1, 3, 11	21	+ 29	11, 3, 1	< 31	- 20
404	284	-286	3, 1, 29	< 39	- 7	2, 2, 28	78	+ 64	1, 3, 13	< 23	+ 15	11, 3, 3	60	+103
408	395	+413	3, 1, 31	90	+ 87	2, 2, 30	55	- 29	1, 3, 15	< 25	+ 30	11, 3, 5	122	+134
4, 0, 12	306	+321	3, 1, 33	41	+ 38	2, 2, 32	< 45	+ 10	1, 3, 17	238	-223	11, 3, 7	49	- 62
4, 0, 16	241	+196	3, 1, 35	< 44	+ 9	422	253	+253	1, 3, 19	< 29	+ 14	11, 3, 9	37	+ 53
4, 0, 20	297	-242	511	184	+184	424	59	- 69	1, 3, 21	133	-102	13, 3, 1	39	+ 65
4, 0, 24	91	+ 75	513	61	- 39	426	69	- 44	1, 3, 23	146	-120	13, 3, 3	39	+ 20
4, 0, 28	46	+ 59	515	333	+427	428	220	+263	1, 3, 25	< 34	+ 10	13, 3, 5	< 39	- 3
4, 0, 32	49	+ 48	517	49	- 50	4, 2, 10	228	+255	1, 3, 27	139	+ 90	13, 3, 7	40	+ 55
602	481	+630	519	149	+157	4, 2, 12	140	+133	1, 3, 29	67	- 67	13, 3, 9	28	- 9
606	88	- 18	5, 1, 11	136	-112	4, 2, 14	256	-233	1, 3, 31	43	- 7	13, 3, 11	< 41	- 30
6, 0, 10	< 21	- 41	5, 1, 13	152	-132	4, 2, 16	164	-166	1, 3, 33	< 44	- 27	040	446	+558
6, 0, 14	311	-269	5, 1, 15	39	- 44	4, 2, 18	< 31	+ 5	331	178	-148	044	514	+593
6, 0, 18	88	+ 80	5, 1, 17	111	+ 95	4, 2, 20	120	+ 84	333	245	-213	048	254	-237
6, 0, 22	213	-192	5, 1, 19	228	-213	4, 2, 22	< 34	- 2	335	294	+271	0, 4, 12	442	+515
6, 0, 26	63	+ 57	5, 1, 21	66	+ 75	4, 2, 24	135	+124	337	111	+107	0, 4, 16	44	+ 76
6, 0, 30	28	- 11	5, 1, 23	115	+ 3	4, 2, 26	125	+ 87	339	26	+ 53	0, 4, 20	196	+154
800	84	- 78	5, 1, 25	77	+ 73	4, 2, 28	27	+ 36	3, 3, 11	206	-190	0, 4, 24	115	+ 75
804	< 14	- 16	5, 1, 27	< 37	+ 11	4, 2, 30	< 41	- 22	3, 3, 13	100	+100	0, 4, 28	128	+106
808	207	-185	5, 1, 29	< 38	+ 8	620	< 13	+ 38	3, 3, 15	54	- 46	0, 4, 32	42	- 46
8, 0, 12	149	-139	5, 1, 31	< 41	+ 13	622	79	+107	3, 3, 17	118	-117	0, 4, 36	< 49	+ 32
8, 0, 16	68	- 79	711	79	+ 82	624	290	+318	3, 3, 19	116	-118	242	123	-111
8, 0, 20	29	+ 34	713	191	+193	626	15	+ 41	3, 3, 21	81	+ 59	244	346	+321
8, 0, 24	< 34	- 28	715	203	+205	628	250	-289	3, 3, 23	78	+ 58	246	23	- 15
8, 0, 28	< 60	- 34	717	60	+ 73	6, 2, 10	110	-105	3, 3, 25	< 35	+ 2	248	160	-159
10, 0, 2	170	+159	719	111	+ 75	6, 2, 12	214	+199	3, 3, 27	36	- 37	2, 4, 10	240	-228
10, 0, 6	175	-112	7, 1, 11	< 28	- 30	6, 2, 14	64	- 77	3, 3, 29	< 39	+ 23	2, 4, 12	104	- 96
10, 0, 10	< 48	- 22	7, 1, 13	67	- 80	6, 2, 16	81	- 70	3, 3, 31	< 41	- 11	2, 4, 14	137	+134
10, 0, 14	< 50	- 19	7, 1, 15	< 31	- 10	6, 2, 18	66	+ 85	3, 3, 33	< 45	- 8	2, 4, 16	< 24	- 6
10, 0, 18	149	+ 97	7, 1, 17	106	+ 86	6, 2, 20	144	+119	3, 3, 35	< 46	- 25	2, 4, 18	< 25	+ 2
10, 0, 22	78	- 95	7, 1, 19	214	+178	6, 2, 22	42	+ 60	5, 3, 1	30	+ 43	2, 4, 20	< 28	- 5
10, 0, 26	< 61	- 2	7, 1, 21	116	+114	6, 2, 24	< 34	- 10	533	88	+100	2, 4, 22	39	- 49
12, 0, 0	261	-238	7, 1, 23	54	+ 9	6, 2, 26	38	- 11	535	380	-469	2, 4, 24	118	- 99
12, 0, 4	< 31	+ 13	7, 1, 25	57	+ 35	6, 2, 28	38	+ 22	537	235	-261	2, 4, 26	85	- 77
12, 0, 8	147	- 82	7, 1, 27	< 43	- 1	6, 2, 30	< 39	- 23	539	111	-120	2, 4, 28	63	+ 57
12, 0, 12	< 56	- 46	7, 1, 29	< 45	- 19	822	70	- 65	5, 3, 11	171	-194	2, 4, 30	< 36	+ 5
12, 0, 16	125	-104	911	42	- 73	824	200	-249	5, 3, 13	68	- 79	2, 4, 32	< 38	- 30
12, 0, 20	57	+ 30	913	163	-165	826	< 19	- 19	5, 3, 15	< 28	- 11	440	58	+ 42
14, 0, 2	< 57	+ 2	915	46	+ 28	828	27	+ 36	5, 3, 17	35	- 63	442	142	-137
14, 0, 6	< 58	0	917	156	-148	8, 2, 10	66	- 51	5, 3, 19	< 32	- 46	444	208	+178
14, 0, 10	< 59	+ 1	919	42	+ 60	8, 2, 12	182	+161	5, 3, 21	103	- 91	446	< 20	+ 16
14, 0, 14	< 60	+ 15	9, 1, 11	42	- 10	8, 2, 14	40	+ 56	5, 3, 23	34	- 42	448	22	- 40
16, 0, 0	< 63	- 81	9, 1, 13	< 50	+ 8	8, 2, 16	< 27	- 8	5, 3, 25	< 37	+ 31	4, 4, 10	263	-267
16, 0, 4	< 63	+ 24	9, 1, 15	< 51	+ 22	8, 2, 18	< 28	+ 2	5, 3, 27	< 39	+ 51	4, 4, 12	342	+336
111	106	- 77	9, 1, 17	< 53	+ 34	8, 2, 20	61	+ 72	5, 3, 29	116	- 94	4, 4, 14	157	-176
113	216	+162	9, 1, 19	78	- 84	8, 2, 22	< 31	- 5	5, 3, 31	< 42	- 34	4, 4, 16	< 27	+ 3
115	131	- 87	9, 1, 21	57	+ 42	8, 2, 24	< 33	+ 27	731	26	+ 36	4, 4, 18	< 27	+ 3
117	326	-297	9, 1, 23	< 59	- 16	8, 2, 26	< 35	- 31	733	193	-207	4, 4, 20	< 29	- 8
119	82	+ 60	11, 1, 1	< 32	- 34	10, 2, 0	76	- 62	735	216	+194	4, 4, 22	68	+ 61
1, 1, 11	268	-257	11, 1, 3	< 56	- 62	10, 2, 2	66	+ 67	737	148	-164	4, 4, 24	42	+ 3
1, 1, 13	182	+168	11, 1, 5	< 57	+ 45	10, 2, 4	80	+ 78	739	57	- 62	4, 4, 26	139	- 95
1, 1, 15	276	+267	11, 1, 7	< 57	+ 19	10, 2, 6	66	+ 70	7, 3, 11	< 28	- 22	4, 4, 28	81	+ 72
1, 1, 17	314	+278	024	188	+151	10, 2, 8	95	- 75	7, 3, 13	144	+ 95	4, 4, 30	38	- 11
1, 1, 19	133	+123	026	591	-668	10, 2, 10	178	+165	7, 3, 15	77	+ 91	4, 4, 32	< 39	- 7
1, 1, 21	176	+123	0, 2, 10	443	+468	10, 2, 12	143	+113	7, 3, 17	112	+122	4, 4, 34	80	- 21
1, 1, 23	< 35	0	0, 2, 14	118	-119	10, 2, 14	160	+150	7, 3, 19	84	- 78	642	< 18	+ 5

Table 8 (cont.)

hk	F _{mean}	F _{calc}	hk	F _{mean}	F _{calc}	hk	F _{mean}	F _{calc}	hk	F _{mean}	F _{calc}	hk	F _{mean}	F _{calc}
644	77	- 92	3, 5, 13	31	- 52	2, 6, 22	< 30	+ 15	1, 7, 25	35	- 30	0, 8, 24	< 41	0
646	208	+222	3, 5, 15	168	+154	2, 6, 24	< 32	+ 8	1, 7, 27	63	+ 45	282	88	+ 93
648	77	-115	3, 5, 17	153	+134	2, 6, 26	132	-102	1, 7, 29	< 39	- 50	284	210	+203
6, 4, 10	267	-293	3, 5, 19	< 25	+ 7	2, 6, 28	55	+ 63	1, 7, 31	< 41	+ 27	286	145	+155
6, 4, 12	39	+ 45	3, 5, 21	33	+ 4	2, 6, 30	< 38	+ 9	371	385	+425	288	77	- 93
6, 4, 14	58	+ 58	3, 5, 23	84	+ 79	2, 6, 32	40	+ 41	373	258	+277	2, 8, 10	< 32	- 8
6, 4, 16	108	+103	3, 5, 25	< 29	- 4	2, 6, 34	41	- 27	375	55	- 76	2, 8, 12	184	-177
6, 4, 18	108	- 80	3, 5, 27	< 30	+ 34	2, 6, 36	< 42	+ 6	377	95	+ 63	2, 8, 14	115	-108
6, 4, 20	< 31	+ 20	3, 5, 29	60	- 63	462	37	- 50	379	< 22	+ 39	2, 8, 16	128	+109
6, 4, 22	< 35	- 37	3, 5, 31	89	+ 98	464	108	-110	3, 7, 11	143	+136	2, 8, 18	71	- 79
6, 4, 24	36	- 56	3, 5, 33	46	+ 64	466	210	+236	3, 7, 13	192	-174	2, 8, 20	90	- 99
6, 4, 26	36	- 55	3, 5, 35	< 36	- 6	468	134	+ 96	3, 7, 15	194	-165	2, 8, 22	< 39	+ 12
5, 4, 28	36	- 13	551	230	+237	4, 6, 10	139	+118	3, 7, 17	70	+ 62	2, 8, 24	40	- 43
6, 4, 30	< 39	+ 29	553	133	-142	4, 6, 12	< 25	+ 35	3, 7, 19	31	+ 54	2, 8, 26	42	+ 33
840	< 29	- 43	555	58	+ 49	4, 6, 14	125	-119	3, 7, 21	39	- 51	2, 8, 28	< 45	- 13
842	215	-248	557	54	- 64	4, 6, 16	55	+ 49	3, 7, 23	42	- 62	480	194	+182
844	80	- 89	559	32	+ 47	4, 6, 18	188	-141	3, 7, 25	90	+ 96	482	183	-187
846	86	+ 89	5, 5, 11	131	+117	4, 6, 20	< 30	+ 3	3, 7, 27	63	+ 62	484	95	+ 98
848	41	- 61	5, 5, 13	35	- 56	4, 6, 22	115	+112	3, 7, 29	< 38	- 14	486	< 30	- 41
8, 4, 10	28	+ 20	5, 5, 15	159	-135	4, 6, 24	90	+ 75	3, 7, 31	< 40	+ 14	488	28	- 59
8, 4, 12	126	-116	5, 5, 17	< 24	+ 22	4, 6, 26	74	+ 64	571	< 21	- 3	4, 8, 10	169	-151
8, 4, 14	31	- 45	5, 5, 19	102	- 80	4, 6, 28	< 36	- 21	573	96	+ 91	4, 8, 12	< 33	- 41
8, 4, 16	35	- 32	5, 5, 21	77	+ 86	4, 6, 30	< 39	+ 3	575	81	- 85	4, 8, 14	228	-250
8, 4, 18	99	- 65	5, 5, 23	66	- 72	660	450	+537	577	254	-277	4, 8, 16	< 35	+ 33
8, 4, 20	< 30	- 20	5, 5, 25	38	+131	662	38	- 30	579	117	-122	4, 8, 18	33	+ 43
8, 4, 22	< 32	- 26	5, 5, 27	< 32	+ 15	654	57	+ 64	5, 7, 11	104	-108	4, 8, 20	94	+ 76
8, 4, 24	< 34	- 13	5, 5, 29	33	- 19	666	< 26	+ 42	5, 7, 13	70	- 66	4, 8, 22	< 39	- 33
8, 4, 26	50	- 72	5, 5, 31	< 34	- 22	668	< 26	- 39	5, 7, 15	58	+ 58	4, 8, 24	< 41	+ 37
8, 4, 28	< 37	- 29	751	83	+ 70	6, 6, 10	< 27	+ 22	5, 7, 17	174	-160	682	44	- 59
10, 4, 2	28	- 14	753	28	- 32	6, 6, 12	53	+ 71	5, 7, 19	< 32	+ 43	684	< 27	- 30
10, 4, 4	31	+ 50	755	40	+ 54	6, 6, 14	< 30	+ 11	5, 7, 21	< 34	+ 17	686	74	- 80
10, 4, 6	31	+ 54	757	110	+ 95	6, 6, 16	162	+142	5, 7, 23	< 36	- 40	688	27	- 60
10, 4, 8	77	+102	759	199	+208	6, 6, 18	31	- 7	5, 7, 25	< 37	+ 10	6, 8, 10	< 29	- 41
10, 4, 10	111	-117	7, 5, 11	100	- 89	6, 6, 20	< 32	+ 16	5, 7, 27	< 38	+ 8	6, 8, 12	< 31	+ 4
10, 4, 12	< 33	- 20	7, 5, 13	101	-102	6, 6, 22	< 34	+ 5	5, 7, 29	54	- 42	6, 8, 14	43	+ 43
10, 4, 14	56	+ 57	7, 5, 15	171	+171	6, 6, 24	126	+106	5, 7, 31	< 42	- 15	6, 8, 16	92	+ 82
10, 4, 16	34	- 62	7, 5, 17	< 28	- 30	6, 6, 26	38	- 11	771	146	+118	6, 8, 18	< 36	+ 13
10, 4, 18	< 36	- 7	7, 5, 19	< 30	+ 46	862	< 23		773	35	+ 60	6, 8, 20	< 36	- 2
12, 4, 0	34	- 67	7, 5, 21	< 31	+ 38	864	27	- 36	775	< 27	- 8	6, 8, 22	< 37	- 30
12, 4, 2	34	+ 43	7, 5, 23	< 32	+ 4	866	92	- 86	777	230	-212	6, 8, 24	< 38	- 27
12, 4, 4	102	- 90	7, 5, 25	62	+ 45	868	94	+ 88	779	93	+ 85	6, 8, 26	< 40	- 44
12, 4, 6	< 35	+ 16	7, 5, 27	31	- 41	8, 6, 10	< 27	- 27	7, 7, 11	30	- 39	880	58	- 83
12, 4, 8	< 35	+ 18	7, 5, 29	< 35	- 10	8, 6, 12	< 28	+ 2	7, 7, 13	34	+ 45	882	194	-199
12, 4, 10	36	- 58	951	28	+ 5	8, 6, 14	< 29	+ 34	7, 7, 15	< 31	+ 16	884	< 27	- 52
12, 4, 12	115	-110	953	< 26	+ 1	8, 6, 16	< 30	0	7, 7, 17	188	+163	886	< 27	+ 28
12, 4, 14	36	- 31	955	< 26	- 8	8, 6, 18	< 32	+ 30	7, 7, 19	50	+ 54	888	< 28	+ 4
12, 4, 16	< 38	- 17	957	181	-189	8, 6, 20	< 33	- 9	7, 7, 21	< 34	- 22	8, 8, 10	< 30	+ 4
14, 4, 2	< 38	+ 3	959	184	+221	8, 6, 22	35	- 37	7, 7, 23	39	- 60	8, 8, 12	< 30	+ 5
14, 4, 4	54	- 69	9, 5, 11	< 27	+ 14	8, 6, 24	49	+ 70	7, 7, 25	< 38	+ 13	8, 8, 14	145	-136
14, 4, 6	38	+ 2	9, 5, 13	< 28	- 36	10, 6, 0	75	+ 95	971	161	-129	8, 8, 16	< 33	- 23
14, 4, 8	< 40	+ 2	9, 5, 15	146	-132	10, 6, 2	79	+ 98	973	115	+113	8, 8, 18	32	+ 7
151	237	-239	9, 5, 17	< 29	+ 5	10, 6, 4	33	- 34	975	30	+ 44	8, 8, 20	< 36	- 39
153	23	+ 18	11, 5, 1	< 29	- 14	10, 6, 6	33	+ 27	977	30	- 29	8, 8, 22	70	- 61
155	130	- 94	11, 5, 3	< 29	+ 26	10, 6, 8	< 33	+ 17	979	30	+ 12	8, 8, 24	< 39	- 21
157	94	+ 94	062	470	-562	10, 6, 10	47	+ 50	9, 7, 11	43	+ 60	10, 8, 2	< 31	+ 9
159	186	-173	066	315	-235	10, 6, 12	47	+ 74	9, 7, 13	80	+ 77	10, 8, 4	< 32	+ 17
1, 5, 11	194	-185	0, 6, 10	197	+176	10, 6, 14	< 37	+ 37	9, 7, 15	29	- 20	12, 8, 0	< 31	- 22
1, 5, 13	297	+285	0, 6, 14	259	+218	10, 6, 16	< 38	+ 37	9, 7, 17	35	- 60	12, 8, 2	< 29	+ 20
1, 5, 15	153	+142	0, 6, 18	< 27	+ 11	10, 6, 18	36	+ 48	9, 7, 19	< 37	+ 30	12, 8, 4	46	- 27
1, 5, 17	32	- 43	0, 6, 22	136	+123	10, 6, 20	< 40	- 54	11, 7, 1	< 31	+ 17	12, 8, 6	38	+ 20
1, 5, 19	189	+164	0, 6, 26	74	- 55	12, 6, 2	< 37	+ 61	11, 7, 3	< 34	+ 13	12, 8, 8	< 38	- 24
1, 5, 21	55	- 51	0, 6, 30	40	- 25	12, 6, 4	< 38	- 30	11, 7, 5	83	+ 97	12, 8, 10	< 38	- 24
1, 5, 23	44	+ 34	0, 6, 34	40	+ 61	12, 6, 6	< 38	- 6	11, 7, 7	34	- 39	191	112	+112
1, 5, 25	77	- 60	0, 6, 38	44	+ 55	171	123	-114	11, 7, 9	< 35	+ 22	193	131	+139
1, 5, 27	41	- 32	260	19	- 20	173	114	-138	11, 7, 11	< 35	- 37	195	195	-202
1, 5, 29	67	+ 56	262	282	-276	175	485	-540	13, 7, 1	< 38	- 20	197	180	+154
1, 5, 31	38	+ 15	264	74	- 78	177	17	+ 32	13, 7, 3	38	+ 58	199	51	- 16
1, 5, 33	< 34	- 7	266	33	- 37	179	20	+ 21	13, 7, 5	38	+ 61	1, 9, 11	119	-121
1, 5, 35	< 36	+ 19	268	254	+256	1, 7, 11	22	- 53	13, 7, 7	< 39	+ 13	1, 9, 13	< 35	- 55
351	< 15	+ 19	2, 6, 10	246	-225	1, 7, 13	63	+ 56	080	66	- 65	1, 9, 15	118	- 88
353	197	+191	2, 6, 12	326	+302	1, 7, 15	< 26	+ 34	084	94	+ 79	1, 9, 17	71	- 62
355	221	-195	2, 6, 14	123	-127	1, 7, 17	48	- 64	088	295	+215	1, 9, 19	116	+102
357	500	+617	2, 6, 16	67	+ 75	1, 7, 19	256	-212	0, 8, 12	314	+232	1, 9, 21	38	- 60
359	425	+449	2, 6, 18	91	- 93	1, 7, 21	224	-184	0, 8, 16	< 37	+ 46	1, 9, 23	< 42	+ 14
3, 5, 11	121	-118	2, 6, 20	169	-142	1, 7, 23	38	- 9	0, 8, 20	35	- 28	1, 9, 25	< 43	+ 43

Table 8 (cont.)

hkℓ	F _{meas}	F _{calc}	hkℓ	F _{meas}	F _{calc}	hkℓ	F _{meas}	F _{calc}	hkℓ	F _{meas}	F _{calc}
1, 9, 27	< 45	+ 24	6, 10, 2	68	- 58	0, 12, 0	175	-103	7, 13, 7	< 45	+ 3
391	63	- 70	6, 10, 4	< 31	+ 28	0, 12, 4	91	-111	7, 13, 9	< 45	+ 19
393	271	+302	6, 10, 6	< 32	+ 8	0, 12, 8	334	+233	9, 13, 1	62	+ 62
395	186	+216	6, 10, 8	42	+ 67	0, 12, 12	< 39	- 50	9, 13, 3	39	- 10
397	< 30	0	6, 10, 10	51	+ 75	0, 12, 16	< 41	+ 41	9, 13, 5	< 40	- 2
399	< 32	- 41	6, 10, 12	110	+112	2, 12, 2	51	+ 79	9, 13, 7	< 40	- 3
3, 9, 11	42	+ 79	6, 10, 14	< 35	+ 28	2, 12, 4	54	+ 65	0, 14, 2	78	+104
3, 9, 13	< 37	+ 50	6, 10, 16	97	+114	2, 12, 6	62	+ 53	0, 14, 6	38	- 8
3, 9, 15	< 35	- 15	6, 10, 18	36	- 28	2, 12, 8	88	- 89	0, 14, 10	114	+139
3, 9, 17	< 36	- 39	6, 10, 20	< 39	- 21	2, 12, 10	52	+ 73	0, 14, 14	143	-103
3, 9, 19	142	+178	6, 10, 22	< 41	- 37	2, 12, 12	< 40	- 37	0, 14, 18	< 47	+ 18
3, 9, 21	125	+119	6, 10, 24	80	+ 80	2, 12, 14	109	-109	2, 14, 0	118	+ 97
3, 9, 23	< 41	+ 5	6, 10, 26	< 44	+ 9	2, 12, 16	< 43	+ 18	2, 14, 2	46	+ 64
3, 9, 25	< 43	- 31	8, 10, 2	< 30	+ 14	2, 12, 18	41	- 38	2, 14, 4	65	+ 99
591	< 29	- 14	8, 10, 4	100	+105	2, 12, 20	< 46	- 14	2, 14, 6	39	- 48
593	194	-200	8, 10, 6	< 31	- 20	2, 12, 22	< 47	+ 15	2, 14, 8	40	- 56
595	90	- 97	8, 10, 8	< 32	+ 17	4, 12, 0	101	+ 98	2, 14, 10	< 43	+ 6
597	< 30	+ 19	8, 10, 10	< 32	- 15	4, 12, 2	182	-158	2, 14, 12	< 44	+ 22
599	< 31	- 30	8, 10, 12	< 34	- 16	4, 12, 4	< 32	- 5	2, 14, 14	42	+ 60
5, 9, 11	< 32	+ 10	8, 10, 14	< 35	- 10	4, 12, 6	< 37	- 21	2, 14, 16	< 47	+ 14
5, 9, 13	88	+ 87	8, 10, 16	< 36	- 43	4, 12, 8	< 38	+ 21	2, 14, 18	< 47	- 21
5, 9, 15	< 34	- 24	10, 10, 0	81	+ 99	4, 12, 10	72	- 77	2, 14, 20	45	+ 69
5, 9, 17	< 36	- 41	10, 10, 2	< 31	+ 57	4, 12, 12	117	-131	2, 14, 22	< 50	+ 2
5, 9, 19	< 37	- 14	10, 10, 4	31	- 17	4, 12, 14	66	- 84	4, 14, 2	< 31	- 5
791	121	-127	12, 10, 2	< 31	+ 50	4, 12, 16	< 42	+ 35	4, 14, 4	38	+ 29
793	68	66	12, 10, 4	< 32	- 32	4, 12, 18	< 43	- 47	4, 14, 6	77	- 99
795	33	+ 41	1, 11, 1	111	-119	4, 12, 20	40	+ 42	4, 14, 8	39	- 41
797	34	- 51	1, 11, 3	32	- 31	4, 12, 22	< 45	- 20	4, 14, 10	39	+ 61
799	35	+ 44	1, 11, 5	131	-110	6, 12, 2	28	- 12	4, 14, 12	< 43	- 21
7, 9, 11	36	+ 66	1, 11, 7	47	- 84	6, 12, 4	32	+ 43	6, 14, 0	30	- 11
7, 9, 13	38	+ 56	1, 11, 9	151	-150	6, 12, 6	118	-136	6, 14, 2	< 34	- 10
7, 9, 15	< 41	+ 40	1, 11, 11	36	+ 31	6, 12, 8	< 36	+ 4	6, 14, 4	59	+ 98
7, 9, 17	126	-107	1, 11, 13	72	+ 72	6, 12, 10	83	+ 99	6, 14, 6	< 39	- 9
7, 9, 19	< 45	+ 25	1, 11, 15	38	- 70	6, 12, 12	< 38	- 13	6, 14, 8	< 39	+ 10
991	< 50	- 59	1, 11, 17	39	- 65	6, 12, 14	< 39	- 24	6, 14, 10	< 40	+ 19
993	105	- 86	1, 11, 19	124	- 84	6, 12, 16	< 40	- 6	6, 14, 12	120	+142
995	117	+111	1, 11, 21	< 43	- 50	6, 12, 18	< 41	+ 37	6, 14, 14	< 42	+ 19
997	< 51	+ 24	1, 11, 23	< 46	- 8	8, 12, 0	< 18	- 42	8, 14, 2	< 38	+ 5
999	< 52	+ 53	1, 11, 25	60	- 59	8, 12, 2	50	- 69	8, 14, 4	36	+ 60
9, 9, 11	99	- 88	1, 11, 27	< 49	- 19	8, 12, 4	< 33	- 3	8, 14, 6	< 38	+ 30
9, 9, 13	< 53	+ 49	3, 11, 1	60	+ 11	8, 12, 6	< 35	- 5	1, 15, 1	< 32	+ 18
11, 9, 1	30	+ 12	3, 11, 3	< 33	0	8, 12, 8	< 36	+ 7	1, 15, 3	64	- 60
11, 9, 3	< 39	+ 33	3, 11, 5	32	+ 56	8, 12, 10	47	- 78	1, 15, 5	< 43	0
0, 10, 2	270	-241	3, 11, 7	212	+212	8, 12, 12	< 37	+ 37	1, 15, 7	40	- 55
0, 10, 6	< 33	+ 37	3, 11, 9	197	-211	8, 12, 14	36	- 72	1, 15, 9	< 44	- 57
0, 10, 10	147	+110	3, 11, 11	< 36	- 47	8, 12, 16	< 38	- 11	3, 15, 1	< 32	- 2
0, 10, 14	< 37	+ 63	3, 11, 13	< 37	+ 47	10, 12, 2	23	+ 18	3, 15, 3	53	+ 47
0, 10, 18	< 41	- 56	3, 11, 15	48	+ 79	10, 12, 4	< 24	- 24	3, 15, 5	39	- 55
0, 10, 22	170	+125	3, 11, 17	< 39	- 24	1, 13, 1	< 32	+ 12	3, 15, 7	< 40	+ 26
0, 10, 26	< 47	+ 9	3, 11, 19	< 41	+ 8	1, 13, 3	< 32	- 15	3, 15, 9	40	- 57
2, 10, 0	144	+168	5, 11, 1	< 32	0	1, 13, 5	36	- 50	3, 15, 11	< 42	- 3
2, 10, 2	< 28	+ 29	5, 11, 3	51	- 54	1, 13, 7	222	+198	5, 15, 1	29	- 38
2, 10, 4	< 29	+ 19	5, 11, 5	< 33	- 7	1, 13, 9	37	- 54	5, 15, 3	37	- 16
2, 10, 6	120	-115	5, 11, 7	< 34	- 31	1, 13, 11	77	+ 60	7, 15, 1	< 28	+ 27
2, 10, 8	33	+ 77	5, 11, 9	< 35	+ 23	1, 13, 13	< 42	- 66	7, 15, 3	< 36	+ 33
2, 10, 10	49	- 36	5, 11, 11	< 36	- 45	1, 13, 15	< 43	- 19	0, 16, 0	162	-152
2, 10, 12	120	+101	5, 11, 13	69	- 62	1, 13, 17	101	- 83	0, 16, 4	< 48	+ 56
2, 10, 14	< 38	- 41	5, 11, 15	90	+ 78	1, 13, 19	< 46	- 28	0, 16, 8	< 46	- 41
2, 10, 16	95	+ 74	5, 11, 17	97	- 74	3, 13, 1	135	+128	0, 16, 12	< 47	- 22
2, 10, 18	< 41	+ 9	5, 11, 19	< 41	+ 4	3, 13, 3	< 37	- 20	2, 16, 2	< 30	- 49
2, 10, 20	< 43	- 22	7, 11, 1	< 33	- 11	3, 13, 5	35	+ 52	2, 16, 4	< 30	- 11
2, 10, 22	< 44	- 37	7, 11, 3	< 39	+ 18	3, 13, 7	< 38	+ 7	4, 16, 0	59	- 84
4, 10, 2	110	+109	7, 11, 5	75	+ 74	3, 13, 9	< 38	+ 14	4, 16, 2	58	- 66
4, 10, 4	< 30	- 17	7, 11, 7	< 40	+ 25	3, 13, 11	< 39	- 18	4, 16, 4	< 45	+ 32
4, 10, 6	32	+ 46	7, 11, 9	< 41	+ 2	3, 13, 13	53	- 60	4, 16, 6	< 45	- 29
4, 10, 8	63	- 76	7, 11, 11	139	-122	3, 13, 15	55	+ 67	6, 16, 2	45	- 81
4, 10, 10	62	+ 57	7, 11, 13	57	+ 82	3, 13, 17	< 42	+ 19	6, 16, 4	< 43	+ 30
4, 10, 12	34	+ 44	7, 11, 15	< 45	+ 28	5, 13, 1	< 33	- 28	0, 18, 2	< 49	- 6
4, 10, 14	< 37	+ 5	9, 11, 1	< 21	+ 21	5, 13, 3	36	- 36	0, 18, 6	92	+ 74
4, 10, 16	< 39	+ 49	9, 11, 3	< 39	+ 50	5, 13, 5	135	-125	0, 18, 10	< 50	- 32
4, 10, 18	52	- 50	9, 11, 5	31	- 46	3, 13, 7	< 38	+ 6	0, 20, 0	< 53	- 3
4, 10, 20	38	+ 36	9, 11, 7	45	+ 95	5, 13, 9	< 39	+ 31			
4, 10, 22	40	+ 66	9, 11, 9	46	+ 58	7, 13, 1	< 32	- 15			
4, 10, 24	< 44	- 47	11, 11, 1	39	+ 49	7, 13, 3	< 40	0			
6, 10, 0	320	+304	11, 11, 3	36	- 44	7, 13, 5	96	- 87			

rather insensitive to changes in the electronic structure of the bonds which form it. This bond angle may also be compared with the corresponding angle in the Se_8 molecule. In α -selenium (Burbank, 1951) it is $105.3 \pm 2.3^\circ$ and in β -selenium (Marsh, Pauling and McCullough, 1953) it is $105.7 \pm 0.8^\circ$.

13. Computing Methods

All structure factors (Table 8), least-squares analyses and triple Fourier series were computed on the 604 calculator and associated reproducer, tabulator, etc., International Business Machines. In the methods used, developed in conjunction with the Office of Statistical Services, Massachusetts Institute of Technology, trigonometric and exponential functions were evaluated by power expansions, and four-figure accuracy was maintained throughout. The double Fourier series were summed using Beevers-Lipson strips, subdividing the a, b, and c axes into 60, 60, and 120 parts, respectively. The positions of the contour lines in Figs. 1 and 2 were obtained from the summation totals by graphical interpolation.

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The Crystal Structure of α -Potassium Superoxide

by

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Abstract: The lattice constants of α -potassium superoxide have been re-measured, and the tetragonal unit cell found to be $a = 5.704 \pm 0.005$ and $c = 6.699 \pm 0.005\text{\AA}$ at 25°C . The coordinates have been refined by use of the method of least squares and by triple Fourier series. Geiger-counter methods were used to measure the intensities diffracted by a powder specimen. The oxygen-oxygen bond length is $1.28 \pm 0.02\text{\AA}$, and there are two kinds of closest potassium-oxygen contact, of 2.71 and 2.92 \AA .

Introduction

An understanding of the various kinds of bond which link two oxygen atoms together is likely to provide considerable insight into the mechanism of bond formation by higher members of the VI_b group of elements. These elements are characterized by possession of two s and four p valence electrons. The case of oxygen is simplified by the nonavailability of d orbitals, which appear to be important for sulfur (Abrahams, 1954), selenium (McCullough and Marsh, 1950) and probably also for tellurium. This restriction leaves the wave functions involving only two oxygen atoms more susceptible to exact solution, and hence emphasizes the importance of precise measurements of the molecular constants for such systems.

Accurate determinations of the length of the oxygen-oxygen bond have

now been made in the case of the oxygen molecule (Babcock and Herzberg, 1948), where the distance is $1.2074 \pm 0.0001\text{A}$, Trambarulo, Ghosh, Burrus and Gordy (1953) report $1.278 \pm 0.003\text{A}$ in ozone, Abrahams and Kalnajs (1954) find $1.49 \pm 0.04\text{A}$ in the peroxide ion, and Abrahams, Collin and Lipscomb (1951) measure $1.49 \pm 0.02\text{A}$ in hydrogen peroxide.

A fifth kind of oxygen-oxygen bond exists in the superoxide ion $[\text{O-O}]^-$, and several attempts have been made to measure this bond length. Kasatochkin and Kotov (1937) were the first to elucidate the crystal structure of the α -potassium compound. Using a cylindrical powder camera with unfiltered CuK radiation, and with the sample sealed within glass capillaries, they were able to observe nine single powder lines with a total intensity range of 1 to 10. The structure contains a single parameter of position, and this was varied by discrete steps until the observed structure factors compared most closely with the calculated structure factors. The temperature factors were neglected in this process. The parameter value giving the best agreement was 0.095, corresponding to an oxygen-oxygen bond distance of 1.28A , with an estimated uncertainty of $\pm 0.07\text{A}$.

Two determinations of the length of the oxygen-oxygen bond in sodium superoxide have been reported. Templeton and Dauben (1950) give the distance as $1.33 \pm 0.06\text{A}$ and Zhdanov and Zvonkova as $1.31 \pm 0.03\text{A}$. In this crystal the superoxide ion appears to be disordered, and does not lend itself to a determination of high accuracy.

The crystal structure of potassium superoxide has been reinvestigated by us using more modern methods in the hope of measuring the oxygen-oxygen bond distance therein with greater accuracy.

Experimental

α -Potassium superoxide was prepared by two methods: The first was

similar to Helms and Klemm's (1939) method, in which the two elements are allowed to react in liquid ammonia at -30 to -50°C . This preparation yielded a product of 95 percent purity, calculated as KO_2 . The second method was an adaptation of Kazarnovskii and Raikhshtein's (1947) method, wherein metallic potassium is oxidized at 180°C in a stream of 20 percent oxygen in nitrogen, gradually increasing the oxygen content to 100 percent. After the potassium had been thus calcined in oxygen at 370°C for 8 h., the cooled reaction tube was transferred to a dry box because of the extreme deliquescence of the superoxide, and the powder was then ground and passed through a 325 mesh sieve into smaller tubes. These tubes were flushed with oxygen, sealed, and the powder then annealed at 120°C for 15 h. This material, on analysis, gave 99.1 percent of the theoretical potassium content (K was determined by standard methods), and 99.2 percent of the theoretical oxygen value (determined volumetrically by decomposition of the superoxide with platinum-black). This preparation was used for the determination of the lattice constants and intensities.

The X-ray methods used have previously been described (Abrahams and Kalnajs, 1954). However, to protect the surface of the sample on transferring it from the dry box to the diffractometer, the filled sample-holder was covered with a glass cover slide, and removed only after it was in position inside the protective chamber. The reduced ratio of peak heights of the reflection to background level in the present crystal, as compared with barium peroxide, resulted in an average accuracy in intensity of only ca. 3 percent. An independent check on the accuracy of the observations was made by comparing two sets of structure factors, derived from the intensities in the usual way, and resulting from two different preparations of the superoxide. The usual comparison ratio $\sum ||F_{\text{obs}}(1)| - |F_{\text{obs}}(2)|| \div \sum |F_{\text{obs}}(1)|$ had a value

0.048. CuK α radiation ($\lambda = 1.5418\text{\AA}$) was used throughout. The James and Brindley (1931) atomic form factors for potassium and oxygen were employed. All calculations were carried out on International Business Machines, except for the Fourier series, which were summed using Beever-Lipson strips.

Crystal Data

α -Potassium superoxide, KO_2 ; m.p. 380°C ; $D_{\text{obs}} = 2.158 \text{ gcm}^{-3}$ (Kasatochkin and Kotov, 1937); $D_{\text{calc}} = 2.166 \text{ gcm}^{-3}$; tetragonal with $a = 5.704 \pm 0.005$ and $c = 6.699 \pm 0.005\text{\AA}$. (Kasatochkin and Kotov found 5.70 and 6.72\AA; Helms and Klemm (1939) gave 5.70 and 6.75\AA.) Absent spectra, $(hk\ell)$ only for $h + k$, $k + \ell$, $\ell + h = 2n + 1$. Space group $F4/mmm$ (chosen by Kasatochkin and Kotov). Four formula-molecules per unit cell. Volume of the unit cell is 217.9\AA^3 . Absorption coefficient for CuK α ($\lambda = 1.5418\text{\AA}$) is 181.9 cm^{-1} . Total number of electrons per unit cell, $F(000)$ is 140.

Analysis of the Structure

Kasatochkin and Kotov (1937) demonstrated that the cation in α -potassium superoxide is at $(0, 0, 1/2)$ and the oxygen atoms at $(00z; 00\bar{z})$, and reported the value of z as 0.095. In the present study it was decided to evaluate two additional parameters, the thermal-vibration parameters for each atom. Each of these parameters was assumed to be isotropic, for it had been shown in the isostructural case of barium peroxide that the effect of neglecting this assumption, upon z , was insensible. The refinement process was carried out at first by the method of least squares. The structure factor has the form

$$F(hk\ell) \cdot 8f_{\text{O}} \exp\left\{-B_1\left(\frac{\sin\theta}{\lambda}\right)^2\right\} \cos 2\pi\ell z \begin{matrix} \ell = 2n \\ + \\ \ell = 2n+1 \end{matrix} 4f_{\text{K}} \exp\left\{-B_2\left(\frac{\sin\theta}{\lambda}\right)^2\right\} ,$$

and in the first model adopted, z was given the value 0.095 and B_1 and B_2 were taken as equal to 2.3\AA^2 . This value was obtained by a consideration of the diminution in magnitude of the observed structure factors (Table 1) with in-

creasing angle. In applying the method of least squares, each equation of condition was given unity as its weight. Although intensities were recorded for 39 lines, only 25 were single and used in the least-squares analysis. Three normal equations were thus obtained and solved and the solutions applied to the original parameters. New structure factors could then be calculated, and a new iteration undertaken. Three such iterations produced corrections to the parameters that were smaller than the errors to be feared in them. This was taken as a sign of convergence in the method, and the final parameters were then 0.0955; 3.42 and 3.29\AA^2 , respectively, for z , B_1 and B_2 . The structure factors calculated on the basis of these parameters are given in Table 1, and have a value $R_1 = 0.076$.

All the F_{obs} terms in Table 1 were then used as coefficients in a triple Fourier series to compute the electron density along the line 00z, which contains both the potassium and the oxygen ions (Fig. 1, lower curve). The position of the center of gravity of the electron density profile for oxygen, taken as z , was 0.0955. In case the observed Fourier series gave a value of z in error due to artificial termination, a second series was evaluated, using the corresponding F_{calc} terms in Table 1 (i.e., those resulting from the final set of coordinates derived by the least-squares process). This series is shown in Fig. 1 (upper curve), and the consequent value of z is 0.0957. The true value of z on applying the usual backshift correction is then 0.0953.

Oxygen-Oxygen Bond Length

The average of the values of z obtained by the method of least squares and the triple Fourier series, was assumed to be the closest approximation. The resulting value of $z = 0.0954$ corresponds to the length 1.28Å for the oxygen-oxygen bond in the superoxide ion.

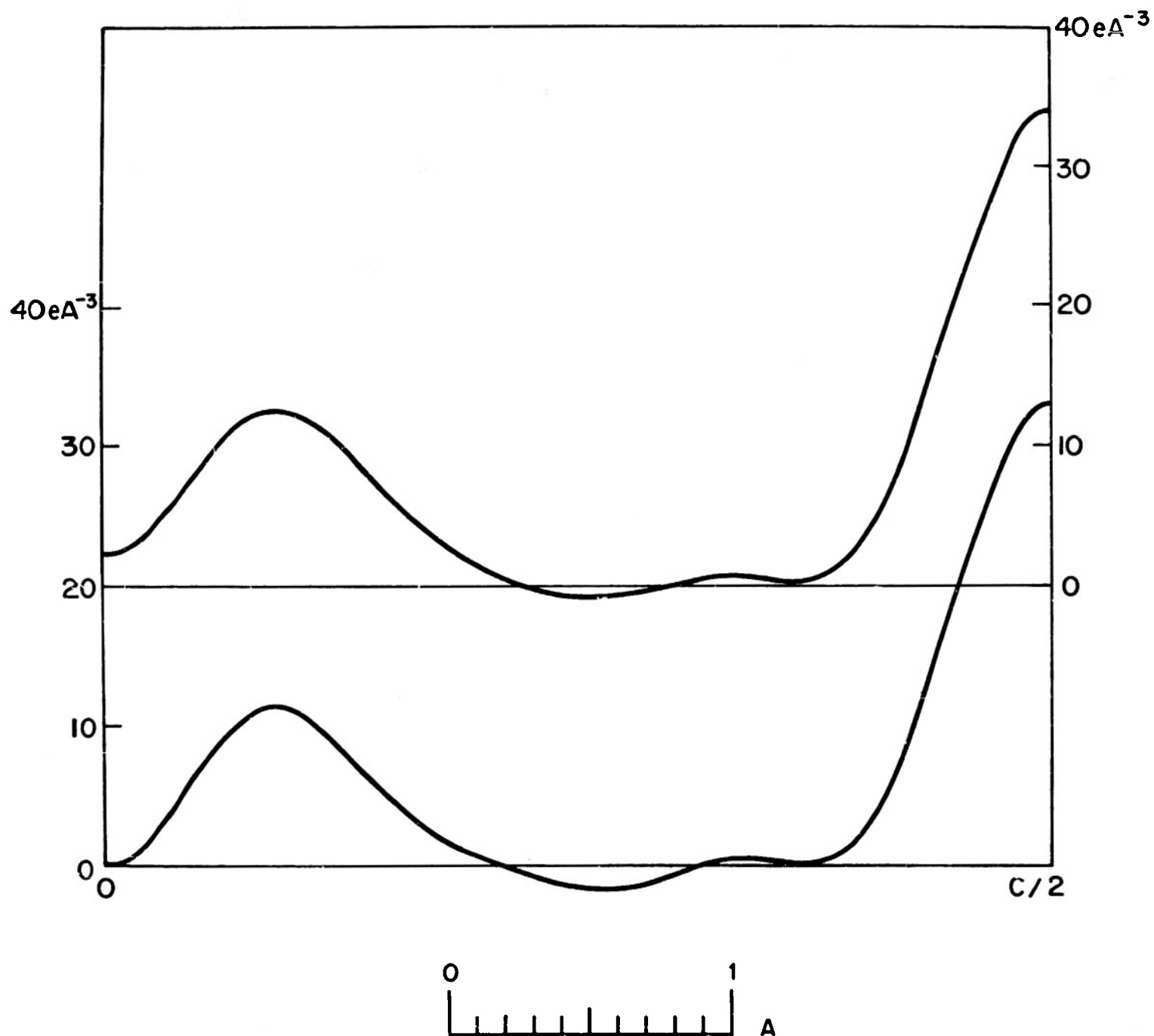


Fig. 1. Electron density profile along the line $00z$, computed with triple Fourier series. Upper curve has calculated $F(hk\ell)$ as coefficients in the series, lower curve has observed $F(hk\ell)$. Left-hand scale refers to lower curve.

Table 1. Observed and calculated structure factors
for α -potassium superoxide.

hkl	d _{obs}	d _{calc}	F _{obs}	F _{calc}	hkl	d _{obs}	d _{calc}	F _{obs}	F _{calc}
111	3.457A	3.456A	17.7	-17.4	404	1.087A	1.086A	13.2	+ 9.3
002	3.350	3.350	74.0	+72.0	135	1.076	1.076	26.3	-25.1
200	2.856	2.853	90.5	+91.6	206	1.040	1.040	6.4	+ 7.4
202	2.172	2.172	53.7	+53.7	244	1.015	1.015	26.5	+ 8.6
220	2.018	2.017	69.0	+68.8	440	1.009	1.009		+21.5
113	1.953	1.954	47.9	-44.8	153	1.001	1.000	14.3	-15.4
311	1.742	1.742	54.4	-13.5	226	0.976	0.977	7.5	+ 6.9
222	1.729	1.728		+42.2	351	0.968	0.968	18.0	- 7.2
004	1.676	1.675	10.5	+15.7	442	0.966	0.966		+15.0
204	1.444	1.444	11.5	+13.1	600	0.950	0.951	33.5	+18.5
400	1.427	1.427	35.0	+43.1	335	0.949	0.949		-18.3
133	1.404	1.404	27.6	-29.2	117	0.931	0.931	20.0	-14.5
331	1.320	1.319	47.3	-10.8	602	0.915	0.916	10.2	+13.2
402	1.313	1.312		+28.1	260	0.902	0.902	26.0	+16.2
224	1.290	1.289	<11.0	+11.6	353	0.897	0.896		-11.9
240	1.276	1.276	70.7	+35.4	406	0.880	0.879	5.5	+ 5.5
115	1.272	1.272		-35.2	262	0.872	0.871	7.6	+11.5
242	1.192	1.192	23.4	+23.6	444	0.864	0.864	<6.0	+ 6.2
333	1.153	1.152	20.9	-21.0	155	0.859	0.859	14.2	-14.0
006	1.116	1.117	6.7	+ 8.0	137	0.845	0.845	13.7	-11.1
151	1.105	1.104	9.7	- 8.5					

Uncertainties in the Parameters

The probable errors in z , B_1 and B_2 , computed by the method of least squares, are $\pm 0.0017A$; ± 0.30 and $\pm 0.13A^2$, respectively. Each oxygen atom then has a probable error of $0.01A$ and hence the probable error in the oxygen-oxygen bond length is $0.02A$. The estimated standard deviation in z , derived by the Fourier series method, was estimated by Cruickshank's (1949) method to be $0.01A$ for the oxygen atom. Again, the estimated standard deviation in the length of the oxygen-oxygen bond is double this, namely, $0.02A$.

The final value for the uncertainty in this bond length is thus $\pm 0.02A$.

Interionic Distances

In this structure, like that of barium peroxide, each cation is surrounded by 10 oxygen atoms. The arrangement of potassium-oxygen contacts is shown in Fig. 2. There are two such sets of smallest contact distances, one of $2.71A$, parallel with c , and one of $2.92A$, in direction approximately normal to c .

Discussion

The two kinds of anion-cation closest contact in this crystal, of 2.71 and $2.92A$, are analogous to the corresponding distances of 2.68 and $2.79A$ in barium peroxide (Abrahams and Kalnajs, 1954). Here, the shorter distance appears to be that of a typical, close, ionic contact between oxygen and potassium. However, the usual values of ionic radii cannot rigidly apply here, since the special shape factor associated with the anion has not been taken into account. It is not apparent why the atoms in this crystal are subject to a rather large thermal vibration, while in the isostructural barium peroxide, the thermal vibration is very small.

It is of interest that the length of the oxygen-oxygen bond in the superoxide ion is the same as in ozone. In the latter, it has been suggested by

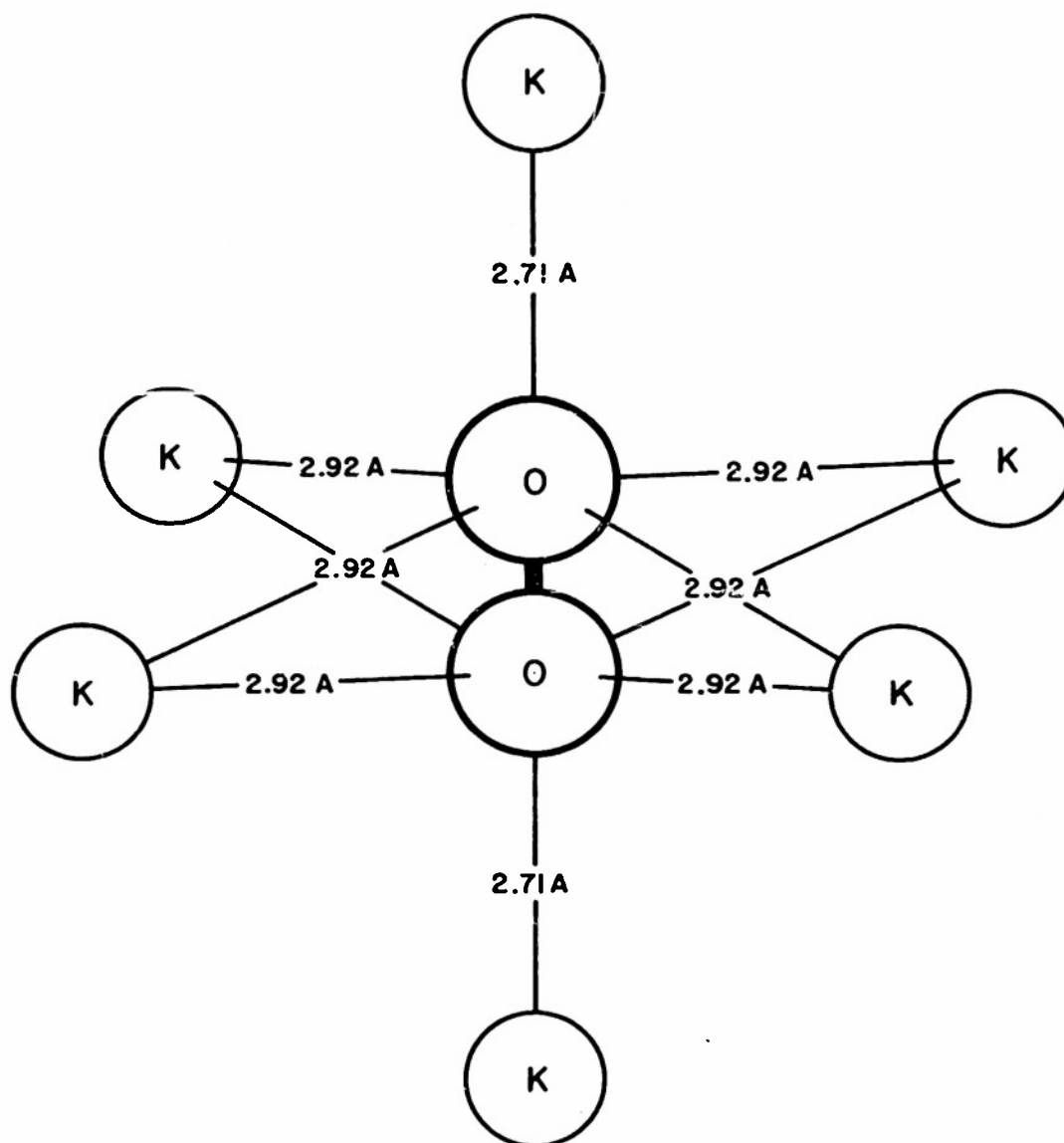


Fig. 2. Octahedral environment of peroxide ion, with closest contact distances indicated.

Trambarulo et al. (1953) that the bond is primarily of 50 percent double character. Thus, the superoxide ion, which contains a three-electron bond, has a length of 1.28 \AA which is close to that of an oxygen-oxygen bond of order 0.5.

It is hence possible to construct a bond order-bond-length relation for oxygen if the bond in the oxygen molecule is regarded as a close approximation to a double bond with length 1.21A, and if the corresponding length in hydrogen peroxide, 1.49A, is taken as a single bond.

Acknowledgement

We would like to thank Professor A. von Hippel for his interest in this work.

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Crystallography of the Tellurium-Iodine System

by

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Abstract: Tellurium tetraiodide is shown to be dimorphous: the tetragonal modification has $a = 16.12 \pm 0.02\text{\AA}$ and $c = 11.20 \pm 0.02\text{\AA}$; space group, $I4_1/amd$. The orthorhombic modification has $a = 13.54 \pm 0.02$, $b = 16.73 \pm 0.02$ and $c = 14.48 \pm 0.02\text{\AA}$; space group $Pnma$. Evidence for the formation of a crystal with composition Tel is presented.

The lattice constants of the terminal members of the tellurium-iodine system are well known. Tellurium (Straumanis, 1940) is hexagonal with $a = 4.456$ and $c = 5.927\text{\AA}$ and iodine is orthorhombic with $a = 4.78$, $b = 7.26$ and $c = 9.79\text{\AA}$ (Heavens and Cheesman, 1950). The only hitherto well-known stoichiometric compound within this system is tellurium tetraiodide. The structure of this compound, hitherto undetermined, is of interest in a study of 2-, 3- and 4-bonded compounds of the VI_b elements currently being carried out in this laboratory. Although the phase diagram of this system had been reported by Jaegar and Menke (1912) and Damiens (1923): it was felt advisable to re-examine the points of composition intermediate between those already known, by X-ray methods.

Experimental

Crystalline tellurium tetraiodide was prepared either by heating tellurium tetrabromide with ethyl iodide (Montignie, 1947) or by reacting the elements by a modification of Damiens (1923) method. In this modification, the elements are

mixed in the requisite proportions, and sealed off in a small-volume Pyrex tube in an atmosphere of nitrogen. Since tellurium melts at 452°C , the tube is heated to ca. 500°C for 2 to 3 h. to ensure completion of the reaction. The black crystals of tellurium tetraiodide have the form of plates and bipyramids. Intermediate compositions were prepared from the melt.

The single crystal X-ray diffraction results were obtained using Weissenberg and precession cameras; the Norelco wide-range diffractometer was used with samples obtainable only in powder form. MoK α radiation was used with the single crystals, CuK α radiation with the powder samples.

Crystal Data for Tetragonal Tellurium Tetraiodide

A few crystals were found with the form of regular bipyramids in one preparation using the method of Montignie (1947). These crystals are tetragonal, with $a = 16.12 \pm 0.04$ and $c = 11.20 \pm 0.02\text{\AA}$, the c axis being the pyramidal axis. Absent spectra, (hkl) when $h + k + l = 2n + 1$; $(hk0)$ when $h = 2n + 1$ and $k = 2n + 1$. Space group is hence uniquely $D_{4h}^{19} - I4_1/amd$. Neither the observed density, nor a confirmatory chemical analysis could be obtained, due to the lack of material. $D_{\text{calc}} = 5.79 \text{ gcm}^{-3}$, assuming 16 formula-molecules per unit cell. Volume of the cell is 2910.3\AA^3 , volume per molecule is 182.0\AA^3 .

Analysis of the Tetragonal Structure

An examination of the intensity distribution in the reciprocal lattice of this crystal reveals the presence of an outstandingly strong superlattice (Fig. 1). These intense reflections correspond to an "inner" pseudo cell, which is also tetragonal, with $a' = 4.03$ and $c' = 5.60\text{\AA}$. In this "inner" cell, the only systematic absences are in (hkl) when $h + k + l = 2n + 1$. The space group of this cell is hence $D_{4h}^{17} - L4/mmm$ or $C_{4h}^5 - I4/m$, and it is related to the real cell by $a' = a/4$ and $c' = c/2$. The "inner" cell must contain one half of a TeI_4 group,

which hence requires at least the tellurium atom to possess a disordered arrangement. There is no indication of disorder in the real cell; however, the disorder in the "inner" cell may be accounted for if the iodine atoms are, for example, at $1/2, 0, 0$ and $0, 1/2, 1/2$ (i.e., related by the body-centering condition + $[1/2, 1/2, 1/2]$) and the tellurium atom is at either $0, 1/2, 0$ or $1/2, 0, 1/2$ (Fig. 2a).

Thus while the iodine

atoms are fully ordered, the tellurium atom has a one-half chance of occupying either of the two possible positions in any cell.

This inner cell distribution may be fitted into the real cell, by placing the tellurium at $0, 1/8, 3/8$ and the iodine at $0, 1/8, 1/8$; $0, 1/8, 5/8$; $1/8, 1/4, 3/8$ (Fig. 2b). This arrangement satisfies the strong reflections very well, but all other reflections are computed to be zero. The resulting value of $R_1 =$

$\sum ||F_{obs}| - |F_{calc}|| \div \sum |F_{obs}|$ is 0.37 for $hk0$ and 0.23 for $h0l$, using the James and Brindley (1931) atomic form factors for tellurium and iodine and

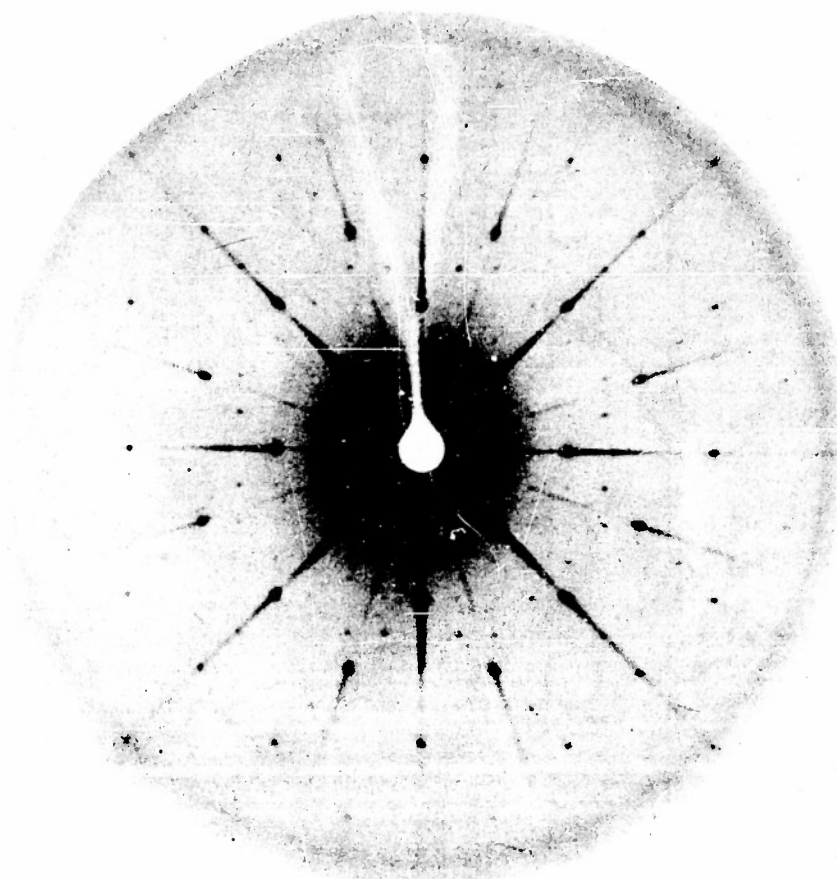
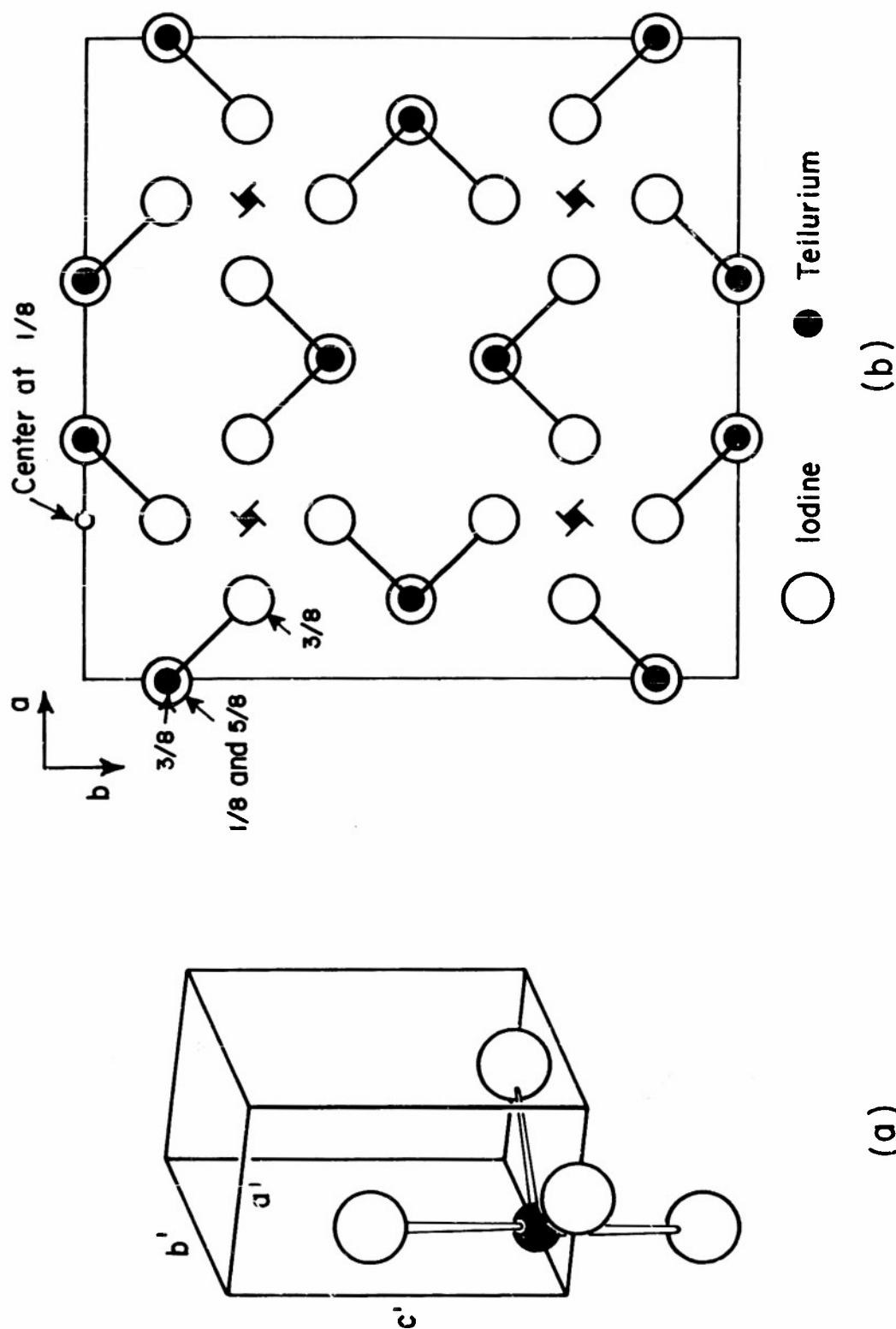


Fig. 1. Precession photograph of the $(hk0)$ layer in tetragonal tellurium tetraiodide.



(a)

(b)

Fig. 2. (a) Arrangement of one TeI_4 molecule in an "inner" cell; (b) distribution of one half of the molecules in the real cell of tetragonal tellurium tetraiodide. The other half is related by centers of symmetry.

$B = 4.0\text{\AA}^2$, in the expression $\exp \left[-B(\sin \theta)/\lambda \right]^2$. This value of B was obtained by assuming the size of the atomic scattering factor at the limit of observation to be 3 percent of the number of electrons in the atom.

The model in Fig. 2b was then refined by the method of least squares, completely evaluating all terms in the normal equations, which were then solved by an iteration process (Morris, 1935). The lowest value of R_1 thus obtained was 0.18 for $hk0$, while for $h0\ell$ the value 0.23 remained unchanged. Complete refinement of the model was not possible because of the rather small range of intensities, and the lack of observed structure factors from upper layers. Attempts at obtaining this extra data were not successful, since the original crystal had been lost, and in subsequent preparations no crystal of the required symmetry was found. The uncertainty in the final coordinates does not warrant a discussion of the structure to which they correspond. However, the closeness of the fit between observed and calculated structure factors appears to be at least good presumptive evidence in favor of these crystals being tellurium tetraiodide.

Crystal Data for Orthorhombic Tellurium Tetraiodide

All preparations except the one referred to above yielded orthorhombic crystals, with lattice constants of $a = 13.54 \pm 0.02$, $b = 16.73 \pm 0.02$ and $c = 14.48 \pm 0.02\text{\AA}$. Absent spectra, $(0k\ell)$ when $k + \ell = 2n + 1$ and $(hk0)$ when $h = 2n + 1$. Space group is $D_{2h}^{16} - Pnma$. D_{obs} is 5.056 gcm^{-3} (Damien, 1923), D_{calc} is 5.145 gcm^{-3} . There are 16 formula-molecules per unit cell. Volume of the cell is 3280.1\AA^3 , volume per molecule is 205.0\AA^3 . Analysis of crystals obtained from the melt gave 81.65 percent iodine: calculated for TeI_4 gives 79.91 percent.

The crystal structure of this modification has not yet been investigated. However, it is clear from a consideration of the effective volume per TeI_4 unit in this crystal, that the packing must be less effective than that shown in Fig. 2b

for the tetragonal modification, for each unit here requires ca. 12 percent more volume.

It has been pointed out by McCullough (1954) that if the new compound is regarded as Te_2I_2 , it would compare closely with the previously known analogous compounds S_2Cl_2 and Se_2Br_2 .

Intermediate Compositions in the Tellurium-Iodide System

The phase diagram of this system has been studied extensively by Damiens (1923) using the method of thermal analysis. There was no unambiguous evidence for any new compound being formed in this study, although Damiens's diagram did contain a peritectic point. Seven compositions in the range between tellurium and tellurium tetraiodide were prepared and their powder diagrams investigated. At the composition with equal parts of tellurium and iodine, a new set of reflections was observed. This composition is very close to Damiens's peritectic point, and corresponds to the molecular formula $\text{Te}_{\frac{1}{2}}\text{I}_{\frac{1}{2}}$.

The new spacings correspond to a crystal having the composition $\text{Te}_{\frac{1}{2}}\text{I}_{\frac{1}{2}}$. This crystal is first formed as a separate phase at a concentration of about 20 percent iodine by weight. At ca. 50 percent the intensities diffracted by the crystal of $\text{Te}_{\frac{1}{2}}\text{I}_{\frac{1}{2}}$ reach a maximum, although there is still a slight indication of the 101 reflection from tellurium. At ca. 70 percent the characteristic pattern of $\text{Te}_{\frac{1}{2}}\text{I}_{\frac{1}{2}}$ diminishes to zero. There is no apparent solid solution of $\text{Te}_{\frac{1}{2}}\text{I}_{\frac{1}{2}}$ in either Te or TeI_4 .

The crystal structure of this apparent compound is complex, and bears no obvious relation to any of the other structures in the system. Attempts at indexing this pattern were without success, although several suggestive relations are apparent. These spacings, and the corresponding intensities, are given in Table 1, together with the spacings of hexagonal tellurium and orthorhombic tellurium tetraiodide for comparison. There are no indications of other crystal

Table 1. Spacings of Te, TeI_n and orthorhombic TeI_4 .

Te	TeI_n	TeI_4 (orthorhombic)
3.88A	7.63A	6.76A
3.24	4.87	5.17
2.36	4.64	3.34
2.24	4.27	3.22
2.09	4.19	2.48
1.98	3.98	2.23
1.93	3.79	2.12*
1.84	3.26	1.91*
1.78	3.24	1.79*
1.76	3.19	1.77*
1.62	3.18	1.67*
1.48	3.08	1.61*
* Composite line.		

formation elsewhere in this system.

In order to determine whether the orthorhombic crystal might possess a transition point, the diffraction pattern was studied at liquid nitrogen temperatures, using the techniques of Abrahams and Kalnajs (1954). The pattern remained essentially unchanged between 25° and -190°C .

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